

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

|  |           |  |
|--|-----------|--|
| <b>(51) International Patent Classification <sup>6</sup> :</b><br><b>C11D 3/386</b>  | <b>A1</b> | <b>(11) International Publication Number:</b> <b>WO 98/13457</b><br><b>(43) International Publication Date:</b> 2 April 1998 (02.04.98)  |
| <b>(21) International Application Number:</b> PCT/US96/15572<br><b>(22) International Filing Date:</b> 27 September 1996 (27.09.96)<br><br><b>(71) Applicant (for all designated States except US):</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).<br><br><b>(72) Inventors; and</b><br><b>(75) Inventors/Applicants (for US only):</b> OHTANI, Ryohei [JP/JP]; 7-19, Ueda-naka-machi, Nishinomiya, Hyogo 663 (JP). MATSUSHITA, Natsuko [JP/JP]; 4-8-11-101, Motoyama-naka-machi, Higashinada-ku, Kobe 651 (JP).<br><br><b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US). |           | <b>(81) Designated States:</b> BR, CA, CN, JP, MX, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).<br><br><b>Published</b><br><i>With international search report.</i> |
| <b>(54) Title:</b> CLEANING COMPOSITIONS COMPRISING A MYCODEXTRANASE<br><br><b>(57) Abstract</b><br><br>The present invention relates to cleaning compositions comprising a mycodextranase enzyme. Such compositions improve specific or broad stain removal, enhanced overall cleaning performance and sanitization of the treated surface.   |           |  |



**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

|    |                          |    |  |    |  |    |                          |
|----|--------------------------|----|--|----|--|----|--------------------------|
| AL | Albania                  | ES | Spain                                    | LS | Lesotho                                      | SI | Slovenia                 |
| AM | Armenia                  | FI | Finland                                  | LT | Lithuania                                    | SK | Slovakia                 |
| AT | Austria                  | FR | France                                   | LU | Luxembourg                                   | SN | Senegal                  |
| AU | Australia                | GA | Gabon                                    | LV | Latvia                                       | SZ | Swaziland                |
| AZ | Azerbaijan               | GB | United Kingdom                           | MC | Monaco                                       | TD | Chad                     |
| BA | Bosnia and Herzegovina   | GE | Georgia                                  | MD | Republic of Moldova                          | TG | Togo                     |
| BB | Barbados                 | GH | Ghana                                    | MG | Madagascar                                   | TJ | Tajikistan               |
| BE | Belgium                  | GN | Guinea                                   | MK | The former Yugoslav<br>Republic of Macedonia | TM | Turkmenistan             |
| BF | Burkina Faso             | GR | Greece                                   | ML | Mali   | TR | Turkey                   |
| BG | Bulgaria                 | HU | Hungary                                  | MN | Mongolia                                     | TT | Trinidad and Tobago      |
| BJ | Benin                    | IE | Ireland                                  | MR | Mauritania                                   | UA | Ukraine                  |
| BR | Brazil                   | IL | Israel                                   | MW | Malawi                                       | UG | Uganda                   |
| BY | Belarus                  | IS | Iceland                                  | MX | Mexico                                       | US | United States of America |
| CA | Canada                   | IT | Italy                                    | NE | Niger  | UZ | Uzbekistan               |
| CF | Central African Republic | JP | Japan                                    | NL | Netherlands                                  | VN | Viet Nam                 |
| CG | Congo                    | KE | Kenya                                    | NO | Norway                                       | YU | Yugoslavia               |
| CH | Switzerland              | KG | Kyrgyzstan                               | NZ | New Zealand                                  | ZW | Zimbabwe                 |
| CI | Côte d'Ivoire            | KP | Democratic People's<br>Republic of Korea | PL | Poland                                       |    |                          |
| CM | Cameroon                 | KR | Republic of Korea                        | PT | Portugal                                     |    |                          |
| CN | China                    | KZ | Kazakhstan                               | RO | Romania                                      |    |                          |
| CU | Cuba                     | LC | Saint Lucia                              | RU | Russian Federation                           |    |                          |
| CZ | Czech Republic           | LI | Liechtenstein                            | SD | Sudan  |    |                          |
| DE | Germany                  | LK | Sri Lanka                                | SE | Sweden                                       |    |                          |
| DK | Denmark                  | LR | Liberia                                  | SG | Singapore                                    |    |                          |
| EE | Estonia                  |    |  |    |  |    |                          |

CLEANING COMPOSITIONS COMPRISING A  
MYCODEXTRANASE

5

TECHNICAL FIELD

10 The present invention relates to cleaning compositions including dishwashing, hard surface cleaning, toilet bowl cleaning and laundry compositions containing a mycodextranase enzyme.

15

BACKGROUND

The overall performance of cleaning compositions for use in washing or cleaning such as dishwashing, hard surface cleaning, toilet bowl cleaning and laundry, is judged by a number of factors, including the ability to remove soils and  
20 the ability to prevent redeposition of the soils or the breakdown product of the soils on the articles being washed.

Food soils are often difficult to remove effectively from a soiled substrate. Highly colored soil derived from  
25 foods and/or beverages for example, tea or coffee, are particularly challenging to remove. Also body soils, especially menstrual fluids are difficult to remove completely and often build up on fabric, which leads to yellowing. The substrates, for example, can be dishes, hard  
30 surfaces, toilet bowls or fabrics.

Enzymes have been added to cleaning compositions as a performance additive to improve cleaning performance. Enzymes can be included in the present cleaning compositions  
35 for a variety of purposes, including removal of

carbohydrate-based stains from surfaces such as textiles, for the prevention of refugee dye transfer in laundering, and for fabric restoration.

- 5 It has now been found that cleaning compositions comprising a mycodextranase enzyme improves specific or broad stain removal, boosts overall cleaning performance and provides sanitization for surfaces treated with the cleaning compositions of the present invention.

10

#### SUMMARY

- The present invention relates to cleaning compositions comprising a mycodextranase enzyme. In further embodiments, the present invention further relates to cleaning  
15 compositions comprising a mycodextranase enzyme in combination with selected detergent ingredients such as other enzymes, surfactants, bleaching agents and the like. Such compositions satisfy the need for a cleaning composition which provide improved specific or broad stain  
20 removal, enhanced overall cleaning performance and sanitization.

#### DETAILED DESCRIPTION

- An essential component of the cleaning compositions of  
25 the present invention is a mycodextranase enzyme.

- This mycodextranase enzyme is incorporated into cleaning compositions in accordance with the present invention at a level of from about 0.00001% to about 1%, preferably from  
30 about 0.0001% to about 0.5%, as a pure enzyme by weight of composition.

- Mycodextranase enzyme, which is 1,3- 1,4-alpha-D-Glucan 4-glucanohydrolase, is any enzyme which hydrolyzes 1,4-  
35 alpha-D-glucosidic linkages in alpha-D-glucans containing

both 1,3- and 1,4- bonds. For example, mycodextranase enzyme hydrolyzes alpha-D-glucans into nigerose and 4-alpha-D-nigerosylglucose. Mycodextranase enzyme does not hydrolyze alpha-D-glucans containing only 1,3- or 1,4- bonds. Also mycodextranase enzyme have no hydrolyzation on the following glucans: alpha-1,4-(amlose), alpha-1,6-(dextran); beta-1,2-; beta-1,3-(laminarin); beta-1,4-(cellulose), beta-1,6-(pustulan). Mycodextranase enzyme is described in the following publications which are hereby incorporated by reference: E.T. Reese and M. Mandels, Canadian Journal of Microbiology, volume 10, pages 103-114 (1964); K.K. Tung, J. Biol. Chem., volume 246, number 22, pages 6722-6735 (1971).

Mycodextranase enzyme can be derived from fungal origin e.g. Penicillium species or can be expressed in any other suitable host organism via cloning techniques known in the art. This mycodextranase enzyme can be produced by the so called wild-type organism or by any host organism in which the gene responsible for the production of the mycodextranase enzyme, has been cloned and expressed.

Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimize their performance efficiency in the cleaning compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability

and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing calcium binding sites to increase chelant stability. Special care must be paid to the cellulases as most of the cellulases have separate binding domains(CBD). Properties of such enzymes can be altered by modifications in these domains.

One preferred type of mycodextranase enzyme is a carbohydrase from the following EC category : EC 3.2.1.61, which are commercially available by Sigma Chemicals. One DU unit liberates 1 micro mole of reducing sugar (measured as glucose) from nigeran per minute at pH 4.5 at 37°C.

#### **Detergent components**

The cleaning compositions of the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition, and the nature of the cleaning operation for which it is to be used.

The cleaning compositions according to the invention can be liquid, paste, gels, bars, tablets, powder or granular forms. Granular compositions can also be in "compact" form, the liquid compositions can also be in a "concentrated" form.

The compositions of the invention may for example, be formulated as hand and machine dishwashing compositions, hand and machine laundry detergent compositions including

laundry additive compositions and compositions suitable for use in the soaking and/or pretreatment of stained fabrics, rinse added fabric softener compositions, and compositions for use in general household hard surface cleaning operations. Compositions containing such mycodextranase enzyme can also be formulated as sanitisation products, contact lenses cleaner and health and beauty care products such as oral/dental care and personal cleaning compositions.

Such compositions containing mycodextranase enzyme can provide fabric cleaning, stain removal, whiteness maintenance, softening, color appearance and dye transfer inhibition when formulated as laundry detergent compositions.

When formulated as compositions for use in manual dishwashing methods the compositions of the invention preferably contain a surfactant and preferably other detergent compounds selected from organic polymeric compounds, suds enhancing agents, group II metal ions, solvents, hydrotropes and additional enzymes.

When formulated as compositions suitable for use in a laundry machine washing method, the compositions of the invention preferably contain both a surfactant and a builder compound and additionally one or more detergent components preferably selected from organic polymeric compounds, bleaching agents, additional enzymes, suds suppressors, dispersants, lime-soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors. Laundry compositions can also contain softening agents, as additional detergent components.

The compositions of the invention can also be used as detergent additive products. Such additive products are



intended to supplement or boost the performance of conventional detergent compositions.

If the composition is a granule, the density of the laundry detergent compositions herein ranges from 400 to 1200 g/litre, preferably 600 to 950 g/litre of composition measured at 20°C.

The "compact" form of the compositions herein is best reflected by density and, in terms of composition, by the amount of inorganic filler salt. Inorganic filler salts are conventional ingredients of detergent compositions in powder form. In conventional detergent compositions, the filler salts are present in substantial amounts, typically 17-35% by weight of the total composition.

In the compact compositions, the filler salt is present in amounts not exceeding 15% of the total composition, preferably not exceeding 10%, most preferably not exceeding 5% by weight of the composition.

The inorganic filler salts, such as meant in the present compositions are selected from the alkali and alkaline-earth-metal salts of sulfates and chlorides.

A preferred filler salt is sodium sulfate.

Liquid detergent compositions according to the present invention can also be in a "concentrated form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents.

Typically the water content of the concentrated liquid detergent is preferably less than 40%, more preferably less than 30%, most preferably less than 20% by weight of the detergent composition.

**Surfactant system**

The cleaning compositions according to the present invention comprise a surfactant system wherein the surfactant can be selected from nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants.

The surfactant is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation are 1% to 35% by weight, most preferably from 1% to 30% by weight of the cleaning composition in accord with the invention.

The surfactant is preferably formulated to be compatible with the mycodextranase enzyme present in the composition. In liquid or gel compositions the surfactant is most preferably formulated such that it promotes, or at least does not degrade, the stability of the mycodextranase enzyme, as well as other optional enzymes, in these compositions.

Preferred surfactant systems to be used according to the present invention comprise one or more of the nonionic and/or anionic surfactants described herein.

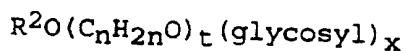
Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 2 to about 25 moles, more preferably from

about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal<sup>TM</sup> CO-630, marketed by the GAF Corporation; and Triton<sup>TM</sup> X-45, X-114, X-100 and X-102, all  
5 marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of primary and secondary  
10 aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and  
15 generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide  
20 per mole of alcohol. About 2 to about 7 moles of ethylene oxide and most preferably from 2 to 5 moles of ethylene oxide per mole of alcohol are present in said condensation products. Examples of commercially available nonionic surfactants of this type include Tergitol<sup>TM</sup> 15-S-9 (the  
25 condensation product of C<sub>11</sub>-C<sub>15</sub> linear alcohol with 9 moles ethylene oxide), Tergitol<sup>TM</sup> 24-L-6 NMW (the condensation product of C<sub>12</sub>-C<sub>14</sub> primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol<sup>TM</sup> 45-9 (the  
30 condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 9 moles of ethylene oxide), Neodol<sup>TM</sup> 23-3 (the condensation product of C<sub>12</sub>-C<sub>13</sub> linear alcohol with 3.0 moles of ethylene oxide), Neodol<sup>TM</sup> 45-7 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 7 moles of ethylene oxide), Neodol<sup>TM</sup> 45-5 (the  
35 condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 5 moles

of ethylene oxide) marketed by Shell Chemical Company, Kyro™ EOB (the condensation product of C<sub>13</sub>-C<sub>15</sub> alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA O30 or O50 (the condensation product of C<sub>12</sub>-C<sub>14</sub> alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6-positions on the preceding saccharide units. The preferred alkylpolyglycosides have the formula



wherein R<sup>2</sup> is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10,

preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or  
5 alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position,  
10 preferably predominately the 2-position.

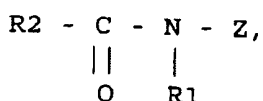
The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the  
15 additional nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion  
20 tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of  
25 ethylene oxide. Examples of compounds of this type include certain of the commercially-available Plurafac<sup>TM</sup> LF404 and Pluronic<sup>TM</sup> surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the  
30 nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and  
35 excess propylene oxide, and generally has a molecular weight

of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic<sup>TM</sup> compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C<sub>8</sub>-C<sub>14</sub> alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C<sub>8</sub>-C<sub>18</sub> alcohol ethoxylates (preferably C<sub>10</sub> avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

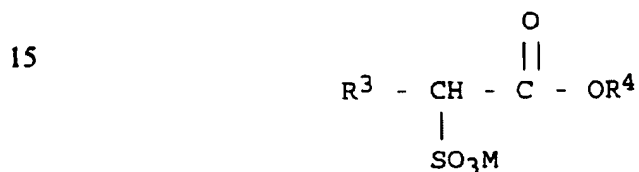
Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula.



wherein R<sup>1</sup> is H, or R<sup>1</sup> is C<sub>1-4</sub> hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R<sup>2</sup> is C<sub>5-31</sub> hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R<sup>1</sup> is methyl, R<sup>2</sup> is a straight C<sub>11-15</sub> alkyl or C<sub>16-18</sub> alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

Suitable anionic surfactants to be used are linear alkyl benzene sulfonate, alkyl ester sulfonate surfactants including linear esters of C<sub>8</sub>-C<sub>20</sub> carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO<sub>3</sub> according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

10 The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula :



20 wherein R<sup>3</sup> is a C<sub>8</sub>-C<sub>20</sub> hydrocarbyl, preferably an alkyl, or combination thereof, R<sup>4</sup> is a C<sub>1</sub>-C<sub>6</sub> hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R<sup>3</sup> is C<sub>10</sub>-C<sub>16</sub> alkyl, and R<sup>4</sup> is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R<sup>3</sup> is C<sub>10</sub>-C<sub>16</sub> alkyl.

30

Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula ROSO<sub>3</sub>M wherein R preferably is a C<sub>10</sub>-C<sub>24</sub> hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C<sub>10</sub>-C<sub>20</sub> alkyl component, more preferably a C<sub>12</sub>-C<sub>18</sub> alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal

cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and  
5 quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C<sub>12</sub>-C<sub>16</sub> are preferred for lower wash temperatures (e.g. below about 50°C) and C<sub>16</sub>-18 alkyl chains are preferred for higher wash  
10 temperatures (e.g. above about 50°C).

Other anionic surfactants useful for deterative purposes can also be included in the cleaning compositions of the present invention. These can include salts (including, for  
15 example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C<sub>8</sub>-C<sub>22</sub> primary or secondary alkanesulfonates, C<sub>8</sub>-C<sub>24</sub> olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline  
20 earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C<sub>8</sub>-C<sub>24</sub> alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl  
25 phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C<sub>12</sub>-C<sub>18</sub> monoesters) and diesters  
30 of sulfosuccinates (especially saturated and unsaturated C<sub>6</sub>-C<sub>12</sub> diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl  
35 polyethoxy carboxylates such as those of the formula



RO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>k</sub>-CH<sub>2</sub>COO-M<sup>+</sup> wherein R is a C<sub>8</sub>-C<sub>22</sub> alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids  
5 and hydrogenated resin acids present in or derived from tall oil.

Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and  
10 Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

15 When included therein, the laundry detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 3% to about 20% by weight of such anionic surfactants.

20 Highly preferred anionic surfactants include alkyl alkoxyated sulfate surfactants hereof are water soluble salts or acids of the formula RO(A)<sub>m</sub>SO<sub>3</sub>M wherein R is an unsubstituted C<sub>10</sub>-C<sub>24</sub> alkyl or hydroxyalkyl group having a C<sub>10</sub>-C<sub>24</sub> alkyl component, preferably a C<sub>12</sub>-C<sub>20</sub> alkyl or  
25 hydroxyalkyl, more preferably C<sub>12</sub>-C<sub>18</sub> alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium,  
30 potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxyated sulfates as well as alkyl propoxyated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and quaternary  
35 ammonium cations such as tetramethyl-ammonium and dimethyl

piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (1.0) sulfate (C<sub>12</sub>-C<sub>18</sub>E(1.0)M), C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (2.25) sulfate (C<sub>12</sub>-C<sub>18</sub>E(2.25)M), C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (3.0) sulfate (C<sub>12</sub>-C<sub>18</sub>E(3.0)M), and C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (4.0) sulfate (C<sub>12</sub>-C<sub>18</sub>E(4.0)M), wherein M is conveniently selected from sodium and potassium.

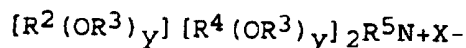
10

The cleaning compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as the nonionic and/or anionic surfactants other than those already described herein.

15

Cationic deterative surfactants suitable for use in the cleaning compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula :

20

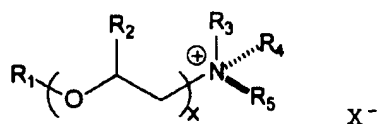


wherein R<sup>2</sup> is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R<sup>3</sup> is selected from the group consisting of -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH(CH<sub>3</sub>)-, -CH<sub>2</sub>CH(CH<sub>2</sub>OH)-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, and mixtures thereof; each R<sup>4</sup> is selected from the group consisting of C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl, benzyl ring structures formed by joining the two R<sup>4</sup> groups, -CH<sub>2</sub>CHOH-CHOHCOR<sup>6</sup>CHOHCH<sub>2</sub>OH wherein R<sup>6</sup> is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R<sup>5</sup> is the same as R<sup>4</sup> or is an alkyl chain wherein the total number of carbon atoms of R<sup>2</sup> plus R<sup>5</sup> is not more than about 18; each y is from 0 to about 10 and the

35

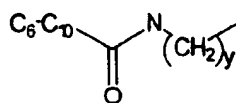
sum of the y values is from 0 to about 15; and X is any compatible anion.

Quaternary ammonium surfactant suitable for the present  
5 invention has the formula (I):



Formula I

whereby R1 is a short chainlength alkyl (C6-C10) or  
10 alkylamidoalkyl of the formula (II) :



Formula II

y is 2-4, preferably 3.

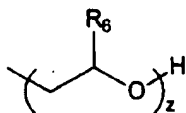
15 whereby R2 is H or a C1-C3 alkyl,

whereby x is 0-4, preferably 0-2, most preferably 0,

whereby R3, R4 and R5 are either the same or different and  
can be either a short chain alkyl (C1-C3) or alkoxyated  
alkyl of the formula III,

20

whereby X- is a counterion, preferably a halide, e.g.  
chloride or methylsulfate.



Formula III

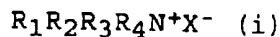
25 R6 is C1-C4 and z is 1 or 2.

Preferred quat ammonium surfactants are those as defined  
in formula I whereby

R1 is C8, C10 or mixtures thereof, x=0,

$R_3, R_4 = \text{CH}_3$  and  $R_5 = \text{CH}_2\text{CH}_2\text{OH}$ .

Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :



wherein  $R_1$  is  $\text{C}_8\text{-C}_{16}$  alkyl, each of  $R_2, R_3$  and  $R_4$  is independently  $\text{C}_1\text{-C}_4$  alkyl,  $\text{C}_1\text{-C}_4$  hydroxy alkyl, benzyl, and  $-(\text{C}_2\text{H}_4\text{O})_x\text{H}$  where  $x$  has a value from 2 to 5, and  $X$  is an anion. Not more than one of  $R_2, R_3$  or  $R_4$  should be benzyl. The preferred alkyl chain length for  $R_1$  is  $\text{C}_{12}\text{-C}_{15}$  particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for  $R_2R_3$  and  $R_4$  are methyl and hydroxyethyl groups and the anion  $X$  may be selected from halide, methosulfate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

- coconut trimethyl ammonium chloride or bromide;
- coconut methyl dihydroxyethyl ammonium chloride or bromide;
- decyl triethyl ammonium chloride;
- decyl dimethyl hydroxyethyl ammonium chloride or bromide;
- $\text{C}_{12}\text{-C}_{15}$  dimethyl hydroxyethyl ammonium chloride or bromide;
- coconut dimethyl hydroxyethyl ammonium chloride or bromide;
- myristyl trimethyl ammonium methyl sulfate;
- lauryl dimethyl benzyl ammonium chloride or bromide;
- lauryl dimethyl (ethenoxy)<sub>4</sub> ammonium chloride or bromide;
- choline esters (compounds of formula (i) wherein  $R_1$  is  $\text{CH}_2\text{-CH}_2\text{-O-C-C}_{12}\text{-C}_{14}$  alkyl and  $R_2R_3R_4$  are methyl).



di-alkyl imidazolines [compounds of formula (i)].

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

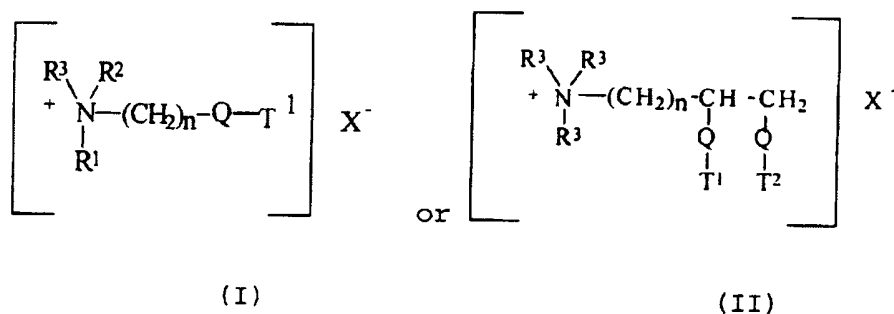
Typical cationic fabric softening components include the water-insoluble quaternary-ammonium fabric softening actives, the most commonly used having been di-long alkyl chain ammonium chloride or methyl sulfate. Preferred cationic softeners among these include the following:

- 1) ditallow dimethylammonium chloride (DTDMAC);
- 2) dihydrogenated tallow dimethylammonium chloride;
- 15 3) dihydrogenated tallow dimethylammonium methylsulfate;
- 4) distearyl dimethylammonium chloride;
- 5) dioleyl dimethylammonium chloride;
- 6) dipalmityl hydroxyethyl methylammonium chloride;
- 20 7) stearyl benzyl dimethylammonium chloride;
- 8) tallow trimethylammonium chloride;
- 9) hydrogenated tallow trimethylammonium chloride;
- 10) C<sub>12-14</sub> alkyl hydroxyethyl dimethylammonium chloride;
- 25 11) C<sub>12-18</sub> alkyl dihydroxyethyl methylammonium chloride;
- 12) di(stearoyloxyethyl) dimethylammonium chloride (DSOEDMAC);
- 13) di(tallowoyloxyethyl) dimethylammonium chloride;
- 30 14) ditallow imidazolinium methylsulfate;
- 15) 1-(2-tallowylamidoethyl)-2-tallowyl imidazolinium methylsulfate.

Biodegradable quaternary ammonium compounds have been presented as alternatives to the traditionally used di-long

alkyl chain ammonium chlorides and methyl sulfates. Such quaternary ammonium compounds contain long chain alk(en)yl groups interrupted by functional groups such as carboxy groups. Said materials and fabric softening compositions containing them are disclosed in numerous publications such as EP-A-0,040,562, and EP-A-0,239,910.

The quaternary ammonium compounds and amine precursors herein have the formula (I) or (II), below :



- wherein Q is selected from -O-C(O)-, -C(O)-O-, -O-C(O)-O-, -NR<sup>4</sup>-C(O)-, -C(O)-NR<sup>4</sup>-;  
 R<sup>1</sup> is (CH<sub>2</sub>)<sub>n</sub>-Q-T<sup>2</sup> or T<sup>3</sup>;  
 R<sup>2</sup> is (CH<sub>2</sub>)<sub>m</sub>-Q-T<sup>4</sup> or T<sup>5</sup> or R<sup>3</sup>;  
 R<sup>3</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl or H;  
 R<sup>4</sup> is H or C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl;  
 T<sup>1</sup>, T<sup>2</sup>, T<sup>3</sup>, T<sup>4</sup>, T<sup>5</sup> are independently C<sub>11</sub>-C<sub>22</sub> alkyl or alkenyl;  
 n and m are integers from 1 to 4; and  
 X<sup>-</sup> is a softener-compatible anion.

Non-limiting examples of softener-compatible anions include chloride or methyl sulfate.

The alkyl, or alkenyl, chain T<sup>1</sup>, T<sup>2</sup>, T<sup>3</sup>, T<sup>4</sup>, T<sup>5</sup> must contain at least 11 carbon atoms, preferably at least 16 carbon atoms. The chain may be straight or branched.

Tallow is a convenient and inexpensive source of long chain alkyl and alkenyl material. The compounds wherein T<sup>1</sup>, T<sup>2</sup>, T<sup>3</sup>, T<sup>4</sup>, T<sup>5</sup> represents the mixture of long chain materials typical for tallow are particularly preferred.

Specific examples of quaternary ammonium compounds suitable for use in the aqueous fabric softening compositions herein include :

- 1) N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
- 2) N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate;
- 3) N,N-di(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
- 4) N,N-di(2-tallowyl-oxy-ethylcarbonyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
- 5) N-(2-tallowyl-oxy-2-ethyl)-N-(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
- 6) N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
- 7) N-(2-tallowyl-oxy-2-oxo-ethyl)-N-(tallowyl-N,N-dimethyl-ammonium chloride; and
- 8) 1,2-ditallowyl-oxy-3-trimethylammoniopropane chloride; and mixtures of any of the above materials.

When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 25%, preferably from about 1% to about 8% by weight of such cationic surfactants.

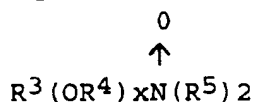
Ampholytic surfactants are also suitable for use in the cleaning compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in

- which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.
- 10 When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.
- 15 Zwitterionic surfactants are also suitable for use in cleaning compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent
- 20 No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants.
- 25 When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.
- 30 Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups
- 35 containing from about 1 to about 3 carbon atoms; water-



soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and  
 5 water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine  
 10 oxide surfactants having the formula



wherein  $R^3$  is an alkyl, hydroxyalkyl, or alkyl phenyl group  
 15 or mixtures thereof containing from about 8 to about 22 carbon atoms;  $R^4$  is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof;  $x$  is from 0 to about 3; and each  $R^5$  is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon  
 20 atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The  $R^5$  groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

25 These amine oxide surfactants in particular include  $C_{10}$ - $C_{18}$  alkyl dimethyl amine oxides and  $C_8$ - $C_{12}$  alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the cleaning compositions of the  
 30 present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

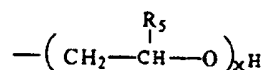
The cleaning composition of the present invention may  
 35 further comprise a cosurfactant selected from the group of primary or tertiary amines. Suitable primary amines for use

herein include amines according to the formula  $R_1NH_2$  wherein  $R_1$  is a  $C_6$ - $C_{12}$ , preferably  $C_6$ - $C_{10}$  alkyl chain or  $R_4X(CH_2)_n$ ,  $X$  is  $-O-$ ,  $-C(O)NH-$  or  $-NH-$ ,  $R_4$  is a  $C_6$ - $C_{12}$  alkyl chain  $n$  is between 1 to 5, preferably 3.  $R_1$  alkyl chains may be  
 5 straight or branched and may be interrupted with up to 12, preferably less than 5 ethylene oxide moieties.

Preferred amines according to the formula herein above are n-alkyl amines. Suitable amines for use herein may be  
 10 selected from 1-hexylamine, 1-octylamine, 1-decylamine and laurylamine. Other preferred primary amines include  $C_8$ - $C_{10}$  oxypropylamine, octyloxypropylamine, 2-ethylhexyl-oxypropylamine, lauryl amido propylamine and amido propylamine.

15

Suitable tertiary amines for use herein include tertiary amines having the formula  $R_1R_2R_3N$  wherein  $R_1$  and  $R_2$  are  $C_1$ - $C_8$  alkylchains or

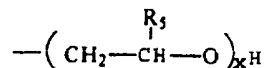


20  $R_3$  is either a  $C_6$ - $C_{12}$ , preferably  $C_6$ - $C_{10}$  alkyl chain, or  $R_3$  is  $R_4X(CH_2)_n$ , whereby  $X$  is  $-O-$ ,  $-C(O)NH-$  or  $-NH-$ ,  $R_4$  is a  $C_4$ - $C_{12}$ ,  $n$  is between 1 to 5, preferably 2-3.  $R_5$  is H or  $C_1$ - $C_2$  alkyl and  $x$  is between 1 to 6.

$R_3$  and  $R_4$  may be linear or branched;  $R_3$  alkyl chains may be  
 25 interrupted with up to 12, preferably less than 5, ethylene oxide moieties.

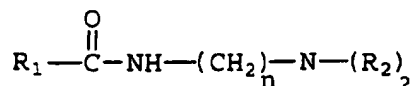
Preferred tertiary amines are  $R_1R_2R_3N$  where  $R_1$  is a  $C_6$ - $C_{12}$  alkyl chain,  $R_2$  and  $R_3$  are  $C_1$ - $C_3$  alkyl or

30



where  $R_5$  is H or  $CH_3$  and  $x = 1-2$ .

Also preferred are the amidoamines of the formula:



wherein  $R_1$  is  $C_6$ - $C_{12}$  alkyl;  $n$  is 2-4,  
preferably  $n$  is 3;  $R_2$  and  $R_3$  is  $C_1$ - $C_4$

5 Most preferred amines of the present invention include 1-octylamine, 1-hexylamine, 1-decylamine, 1-dodecylamine, C8-10oxypropylamine, N coco 1-3diaminopropane, coconutalkyldimethylamine, lauryldimethylamine, lauryl bis(hydroxyethyl)amine, coco bis(hydroxyethyl)amine, lauryl  
10 amine 2 moles propoxylated, octyl amine 2 moles propoxylated, lauryl amidopropyldimethylamine, C8-10 amidopropyldimethylamine and C10 amidopropyldimethylamine. The most preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1-  
15 dodecylamine. Especially desirable are n-dodecyldimethylamine and bishydroxyethylcoconutalkylamine and oleylamine 7 times ethoxylated, lauryl amido propylamine and cocoamido propylamine.

## 20 Conventional detergent enzymes

The cleaning compositions can in addition to mycodextranase enzyme further comprise one or more enzymes which provide cleaning performance and/or fabric care benefits.

25

Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases,  
30 phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases,  $\beta$ -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof.

A preferred combination is a cleaning composition having cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase in  
5 conjunction with one or more plant cell wall degrading enzymes.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will  
10 have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, which discloses fungal cellulase produced from *Humicola insolens*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

15

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800. Other suitable cellulases are cellulases originated from  
20 *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from *Humicola insolens*, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence  
25 disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from *Trichoderma longibrachiatum* described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits.  
30 Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17243.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

Preferred enhancers are substituted phenothiazine and phenoxazine 10-Phenothiazinepropionicacid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substituted syringates (C3-C5 substituted alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said cellulases and/or peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those

which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 Lipase<sup>R</sup> and Lipomax<sup>R</sup> (Gist-Brocades) and Lipolase<sup>R</sup> and Lipolase Ultra<sup>R</sup> (Novo) which have found to be very effective when used in combination with the compositions of the present invention.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE<sup>®</sup> by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE<sup>®</sup>, DURAZYM<sup>®</sup> and

SAVINASE<sup>®</sup> from Novo and MAXATASE<sup>®</sup>, MAXACAL<sup>®</sup>, PROPERASE<sup>®</sup> and MAXAPEM<sup>®</sup> (protein engineered Maxacal) from Gist-Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein.

More preferred is what is called herein "Protease C", which is a variant of an alkaline serine protease from Bacillus in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein. See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 93/18140 A to Novo.

Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo.

In more detail, protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid

for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group  
5 consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO95/10591 and in the patent  
10 application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, filed October 13, 1994.

Also suitable for the present invention are proteases  
15 described in patent applications EP 251 446 and WO91/06637 and protease BLAP<sup>®</sup> described in WO91/02792. The proteolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005%  
20 to 0.1% pure enzyme by weight of the composition.

Amylases ( $\alpha$  and/or  $\beta$ ) can be included for removal of carbohydrate-based stains. WO94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions  
25 which incorporate mutant amylases. See also WO94/18314, Genencor, published August 18, 1994 and WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in cleaning compositions include both  $\alpha$ - and  $\beta$ -amylases.  $\alpha$ -Amylases are known in the art and include  
30 those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylase are stability-enhanced amylases including Purafact Ox Am<sup>®</sup> described in WO 94/18314,  
35 published August 18, 1994 and WO96/05295, Genencor,



published February 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95.

5

Examples of commercial  $\alpha$ -amylases products are Termamyl<sup>®</sup>, Ban<sup>®</sup>, Fungamyl<sup>®</sup> and Duramyl<sup>®</sup>, all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases :  $\alpha$ -amylases characterised by having a specific  
10 activity at least 25% higher than the specific activity of Termamyl<sup>®</sup> at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas<sup>®</sup>  $\alpha$ -amylase activity assay. Other amylolytic enzymes with improved properties with respect to the activity level and  
15 the combination of thermostability and a higher activity level are described in WO95/35382.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and  
20 yeast origin.

Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or  
25 non-purified forms of these enzymes may be used. Also included by definition, are mutants of native enzymes. Mutants can be obtained e.g. by protein and/or genetic engineering, chemical and/or physical modifications of native enzymes. Common practice as well is the expression of  
30 the enzyme via host organisms in which the genetic material responsible for the production of the enzyme has been cloned.

Said enzymes are normally incorporated in the detergent  
35 composition at levels from 0.0001% to 2% of active enzyme by

weight of the detergent composition. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc... containing one enzyme ) or as mixtures of two or more enzymes ( e.g. cogramulates ).

5

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation  
10 scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor  
15 International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985.

20 Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation  
25 techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful Bacillus, sp. AC13 giving proteases, xylanases and  
30 cellulases, is described in WO 9401532 A to Novo.

#### Color care benefits

Technologies which provide a type of color care benefit can also be included. Examples of these technologies are  
35 metallo catalysts for color maintenance. Such metallo

catalysts are described in copending European Patent Application No. 92870181.2.

#### **Bleaching agent**

5 Additional optional detergent ingredients that can be included in the cleaning compositions of the present invention include bleaching agents such as hydrogen peroxide, PB1, PB4 and percarbonate with a particle size of 400-800 microns. These bleaching agent components can  
10 include one or more oxygen bleaching agents and, depending upon the bleaching agent chosen, one or more bleach activators. When present oxygen bleaching compounds will typically be present at levels of from about 1% to about 25%.

15

The bleaching agent component for use herein can be any of the bleaching agents useful for cleaning compositions including oxygen bleaches as well as others known in the art. The bleaching agent suitable for the present invention  
20 can be an activated or non-activated bleaching agent.

One category of oxygen bleaching agent that can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include  
25 magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent Application 740,446, European Patent Application  
30 0,133,354 and U.S. Patent 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxy caproic acid as described in U.S. Patent 4,634,551.

Another category of bleaching agents that can be used  
35 encompasses the halogen bleaching agents. Examples of

hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at 0.5-10%  
5 by weight of the finished product, preferably 1-5% by weight.

The hydrogen peroxide releasing agents can be used in combination with bleach activators such as  
10 tetraacetylenediamine (TAED), nonanoyloxybenzenesulfonate (NOBS, described in US 4,412,934), 3,5,-trimethylhexanoyloxybenzenesulfonate (ISONOBS, described in EP 120,591) or pentaacetylglucose (PAG) or Phenolsulfonate ester of N-nonanoyl-6-aminocaproic acid (NACA-OBS, described  
15 in WO94/28106), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect. Also suitable activators are acylated citrate esters such as disclosed in Copending European Patent Application No. 91870207.7.

20 Useful bleaching agents, including peroxyacids and bleaching systems comprising bleach activators and peroxygen bleaching compounds for use in detergent compositions according to the invention are described in our co-pending  
25 applications USSN 08/136,626, PCT/US95/07823, WO95/27772, WO95/27773, WO95/27774 and WO95/27775.

The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore)  
30 which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Metal-containing catalysts for use in bleach compositions, include cobalt-containing catalysts such as Pentaamine acetate cobalt(III) salts and manganese-containing catalysts such as those described in EPA 549 271; EPA 549 272; EPA 458 397; US 5,246,621; EPA 458 398; US 5,194,416 and US 5,114,611. Bleaching composition comprising a peroxy compound, a manganese-containing bleach catalyst and a chelating agent is described in the patent application No 94870206.3.

10

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, detergent compositions will contain about 0.025% to about 1.25%, by weight, of sulfonated zinc phthalocyanine.

25

#### **Builder system**

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates, alkyl- or alkenyl-succinic acid and fatty acids, materials such as ethylenediamine tetraacetate, diethylene triamine pentamethyleneacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine

35

pentamethylenephosphonic acid. Phosphate builders can also be used herein.

Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B, HS or MAP.

Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ( $\text{Na}_2\text{Si}_2\text{O}_5$ ).

Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates.

Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British  
5 Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include  
10 cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran -cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane -hexacarboxylates and  
15 and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic poly-carboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343. Of the above, the preferred polycarboxylates are  
20 hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Preferred builder systems for use in the present compositions include a mixture of a water-insoluble  
25 aluminosilicate builder such as zeolite A or of a layered silicate (SKS-6), and a water-soluble carboxylate chelating agent such as citric acid.

A suitable chelant for inclusion in the detergent  
30 compositions in accordance with the invention is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium  
35 salt thereof. Examples of such preferred sodium salts of

EDDS include  $\text{Na}_2\text{EDDS}$  and  $\text{Na}_4\text{EDDS}$ . Examples of such preferred magnesium salts of EDDS include  $\text{MgEDDS}$  and  $\text{Mg}_2\text{EDDS}$ . The magnesium salts are the most preferred for inclusion in compositions in accordance with the invention.

5

Preferred builder systems include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid. Preferred builder systems for use in liquid detergent compositions of the present invention are soaps and polycarboxylates.

Other builder materials that can form part of the builder system for use in granular compositions include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.

Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Detergency builder salts are normally included in amounts of from 5% to 80% by weight of the composition preferably from 10% to 70% and most usually from 30% to 60% by weight.

**Suds suppressor**



Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in  
5 finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-  
10 surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

15 A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977.  
20 An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alkanols. Suitable 2-alkyl-alkanols are 2-  
25 butyl-octanol which are commercially available under the trade name Isofol 12 R.  
Such suds suppressor system are described in Copending European Patent application N 92870174.7 filed 10 November, 1992.

30

Especially preferred silicone suds controlling agents are described in Copending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous  
35 silica such as Aerosil<sup>R</sup>.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

5

#### Others

Other components used in cleaning compositions may be employed, such as soil-suspending agents, soil-release agents, optical brighteners, abrasives, bactericides, 10 tarnish inhibitors, coloring agents, and/or encapsulated or non-encapsulated perfumes.

Especially suitable encapsulating materials are water soluble capsules which consist of a matrix of polysaccharide 15 and polyhydroxy compounds such as described in GB 1,464,616.

Other suitable water soluble encapsulating materials comprise dextrans derived from ungelatinized starch acid-esters of substituted dicarboxylic acids such as described 20 in US 3,455,838. These acid-ester dextrans are, preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials include N-Lok manufactured by National Starch. The N-Lok encapsulating material consists 25 of a modified maize starch and glucose. The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

Antiredeposition and soil suspension agents suitable 30 herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid 35 copolymers previously mentioned as builders, as well as

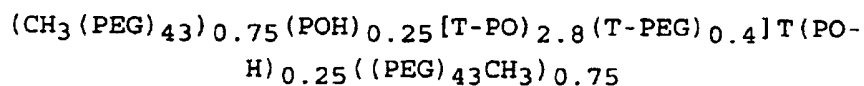
copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, 5 more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2' disulphonate, 10 disodium 4, - 4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino-stilbene-2:2' - disulphonate, disodium 4,4' - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2' - disulphonate, monosodium 4',4'' -bis-(2,4-dianilino-s-triazin-6 15 ylamino)stilbene-2-sulphonate, disodium 4,4' -bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2' - disulphonate, di-sodium 4,4' -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2' disulphonate, di-so-dium 4,4'bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylami-no)stilbene- 20 2,2'disulphonate, sodium 2(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3 - triazole-2''-sulphonate and 4,4'-bis(2-sulphostyryl)biphenyl. Highly preferred brighteners are the specific brighteners of copending European Patent 25 application No. 95201943.8.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 30 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance

on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula



where PEG is  $-(\text{OC}_2\text{H}_4)_n-$ , PO is  $(\text{OC}_3\text{H}_6\text{O})$  and T is  $(\text{pcOC}_6\text{H}_4\text{CO})$ .

Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane 1-2 diol, about 10% by weight ethylene glycol about

13% by weight of dimethyl sulfobenzoic acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3,000. The polyesters and their method of preparation are described in detail in EPA 311 342.

5

Is is well known in the art that free chlorine in tap water rapidly deactivates the enzymes comprised in detergent compositions. Therefore, using chlorine scavenger such as perborate, ammonium sulfate, sodium sulphite or polyethyleneimine at a level above 0.1% by weight of total composition, in the formulas will provide improved through the wash stability of the detergent enzymes. Compositions comprising chlorine scavenger are described in the European patent application 92870018.6 filed January 31, 1992.

15

Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula  $-(CH_2CH_2O)_m(CH_2)_nCH_3$  wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

25  
30

#### Softening agents

Fabric softening agents can also be incorporated into laundry detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the

35

smectite clays disclosed in GB-A-1 400 898 and in USP 5,019,292. Organic fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A1 514 276 and EP-B0 011 340 and their combination with mono C12-  
5 C14 quaternary ammonium salts are disclosed in EP-B-0 026 527 and EP-B-0 026 528 and di-long-chain amides as disclosed in EP-B-0 242 919. Other useful organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0 299 575  
10 and 0 313 146.

Levels of smectite clay are normally in the range from 2% to 20%, more preferably from 5% to 15% by weight, with the material being added as a dry mixed component to the  
15 remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide  
20 materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to the spray dried portion of the composition, although in some instances it may be more convenient to add them as a dry mixed  
25 particulate, or spray them as molten liquid on to other solid components of the composition.

#### Dispersants

The cleaning composition of the present invention can  
30 also contain dispersants : Suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms.

Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 1,000 to 100,000.

5

Especially, copolymer of acrylate and methylacrylate such as the 480N having a molecular weight of 4000, at a level from 0.5-20% by weight of composition can be added in the cleaning compositions of the present invention.

10

The compositions of the invention may contain a lime soap peptiser compound, which has a lime soap dispersing power (LSDP), as defined hereinafter of no more than 8, preferably no more than 7, most preferably no more than 6.

15 The lime soap peptiser compound is preferably present at a level from 0% to 20% by weight.

A numerical measure of the effectiveness of a lime soap peptiser is given by the lime soap dispersant power (LSDP) which is determined using the lime soap dispersant test as described in an article by H.C. Borghetty and C.A. Bergman, J. Am. Oil. Chem. Soc., volume 27, pages 88-90, (1950). This lime soap dispersion test method is widely used by practitioners in this art field being referred to, for example, in the following review articles; W.N. Linfield, Surfactant science Series, Volume 7, page 3; W.N. Linfield, Tenside surf. det., volume 27, pages 159-163, (1990); and M.K. Nagarajan, W.F. Masler, Cosmetics and Toiletries, volume 104, pages 71-73, (1989). The LSDP is the % weight ratio of dispersing agent to sodium oleate required to disperse the lime soap deposits formed by 0.025g of sodium oleate in 30ml of water of 333ppm  $\text{CaCO}_3$  (Ca:Mg=3:2) equivalent hardness.

Surfactants having good lime soap peptiser capability will include certain amine oxides, betaines, sulfobetaines, alkyl ethoxysulfates and ethoxylated alcohols.

5 Exemplary surfactants having a LSDP of no more than 8 for use in accord with the present invention include C<sub>16</sub>-C<sub>18</sub> dimethyl amine oxide, C<sub>12</sub>-C<sub>18</sub> alkyl ethoxysulfates with an average degree of ethoxylation of from 1-5, particularly C<sub>12</sub>-C<sub>15</sub> alkyl ethoxysulfate surfactant with a degree of  
10 ethoxylation of amount 3 (LSDP=4), and the C<sub>14</sub>-C<sub>15</sub> ethoxylated alcohols with an average degree of ethoxylation of either 12 (LSDP=6) or 30, sold under the tradenames Lutensol A012 and Lutensol A030 respectively, by BASF GmbH.

15 Polymeric lime soap peptisers suitable for use herein are described in the article by M.K. Nagarajan, W.F. Masler, to be found in Cosmetics and Toiletries, volume 104, pages 71-73, (1989).

20 Hydrophobic bleaches such as 4-[N-octanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-nonanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-decanoyl-6-aminohexanoyl]benzene sulfonate and mixtures thereof; and nonanoyloxy benzene sulfonate together with hydrophilic /  
25 hydrophobic bleach formulations can also be used as lime soap peptisers compounds.

#### Dye transfer inhibition

The cleaning compositions of the present invention can  
30 also include compounds for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

35 Polymeric dye transfer inhibiting agents



The cleaning compositions according to the present invention also comprise from 0.001% to 10 %, preferably from 0.01% to 2%, more preferably from 0.05% to 1% by weight of polymeric dye transfer inhibiting agents. Said polymeric dye transfer inhibiting agents are normally incorporated into cleaning compositions in order to inhibit the transfer of dyes from colored fabrics onto fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

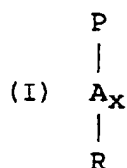
Especially suitable polymeric dye transfer inhibiting agents are polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinylloxazolidones and polyvinylimidazoles or mixtures thereof.

Addition of such polymers also enhances the performance of the enzymes according the invention.

a) Polyamine N-oxide polymers

The polyamine N-oxide polymers suitable for use contain units having the following structure formula :

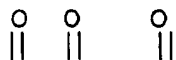
25



30

wherein P is a polymerisable unit, whereto the R-N-O group can be attached to or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.

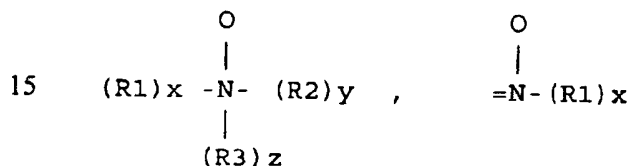
35



A is NC, CO, C, -O-, -S-, -N- ; x is 0 or 1;

5 R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

10 The N-O group can be represented by the following general structures :



20 wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

25 The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

30 Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups.

35 One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyrridine,

pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group  
5 is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit.

10

Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R  
15 group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyrridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the  
20 polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups. Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

25

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters,  
30 polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1  
35 to 1:1000000. However the amount of amine oxide groups

present in the polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a PKa < 10, preferably PKa < 7, more preferred PKa < 6. The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power.

Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

The N-vinylimidazole N-vinylpyrrolidone polymers used in the present invention have an average molecular weight range from 5,000-1,000,000, preferably from 5,000-200,000.

Highly preferred polymers for use in detergent compositions according to the present invention comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000.

The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol 113, "Modern Methods of Polymer

Characterization". Highly preferred N-vinylimidazole N-vinylpyrrolidone copolymers have an average molecular weight range from 5,000 to 50,000; more preferably from 8,000 to 30,000; most preferably from 10,000 to 20,000.

5

The N-vinylimidazole N-vinylpyrrolidone copolymers characterized by having said average molecular weight range provide excellent dye transfer inhibiting properties while not adversely affecting the cleaning performance of detergent compositions formulated therewith.

The N-vinylimidazole N-vinylpyrrolidone copolymer of the present invention has a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4 .

15

#### c) Polyvinylpyrrolidone

The detergent compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12; polyvinylpyrrolidones known to persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696) .

35

d) Polyvinylloxazolidone :

The detergent compositions of the present invention may also utilize polyvinylloxazolidone as a polymeric dye transfer inhibiting agent. Said polyvinylloxazolidones have  
5 an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

10 e) Polyvinylimidazole :

The detergent compositions of the present invention may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles have an average  
15 about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

20 f) Cross-linked polymers :

Cross-linked polymers are polymers whose backbone are interconnected to a certain degree; these links can be of chemical or physical nature, possibly with active groups in the backbone or on branches; cross-linked polymers have been  
25 described in the Journal of Polymer Science, volume 22, pages 1035-1039.

In one embodiment, the cross-linked polymers are made in such a way that they form a three-dimensional rigid  
30 structure, which can entrap dyes in the pores formed by the three-dimensional structure. In another embodiment, the cross-linked polymers entrap the dyes by swelling.

Such cross-linked polymers are described in the co-  
35 pending patent application 94870213.9

**Method of washing**

The compositions of the invention may be used in essentially any washing or cleaning methods, including  
5 soaking methods, pretreatment methods and methods with rinsing steps for which a separate rinse aid composition may be added.

The process described herein comprises contacting  
10 fabrics with a laundering solution in the usual manner and exemplified hereunder.

The process of the invention is conveniently carried out in the course of the cleaning process. The method of  
15 cleaning is preferably carried out at 5°C to 95°C, especially between 10°C and 60°C. The pH of the treatment solution is preferably from 7 to 11.

A preferred machine dishwashing method comprises  
20 treating soiled articles with an aqueous liquid having dissolved or dispensed therein an effective amount of the machine dishwashing or rinsing composition. A conventional effective amount of the machine dishwashing composition means from 8-60 g of product dissolved or dispersed in a  
25 wash volume from 3-10 litres.

According to a manual dishwashing method, soiled dishes are contacted with an effective amount of the dishwashing composition, typically from 0.5-20g (per 25 dishes being  
30 treated). Preferred manual dishwashing methods include the application of a concentrated solution to the surfaces of the dishes or the soaking in large volume of dilute solution of the detergent composition.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

5

In the detergent compositions, the enzymes levels are expressed by pure enzyme by weight percentage of the total composition and the detergent ingredients are expressed by weight percentage of the total compositions, unless  
10 otherwise specified. The abbreviated component identifications therein have the following meanings:

|                                  |  |
|----------------------------------|--|
| LAS                              | : Sodium linear C <sub>12</sub> alkyl benzene sulphonate   |
| TAS                              | : Sodium tallow alkyl sulfate  |
| C <sub>X</sub> YAS               | : Sodium C <sub>1X</sub> - C <sub>1Y</sub> alkyl sulfate   |
| C <sub>25</sub> E <sub>Y</sub>   | : A C <sub>12</sub> -C <sub>15</sub> predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide                           |
| C <sub>X</sub> YE <sub>Z</sub>   | : A C <sub>1X</sub> - C <sub>1Y</sub> predominantly linear primary alcohol condensed with an average of Z moles of ethylene oxide                          |
| C <sub>X</sub> YE <sub>Z</sub> S | : C <sub>1X</sub> - C <sub>1Y</sub> sodium alkyl sulfate condensed with an average of Z moles of ethylene oxide per mole                                   |
| QAS                              | : R <sub>2</sub> .N <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH) with R <sub>2</sub> = C <sub>12</sub> -C <sub>14</sub> |



|              |   |
|--------------|---|
| Soap         | : Sodium linear alkyl carboxylate derived from a 80/20 mixture of tallow and coconut oils.  |
| Nonionic     | : C <sub>13</sub> -C <sub>15</sub> mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5 sold under the tradename Plurafac LF404 by BASF GmbH. |
| CFAA         | : C <sub>12</sub> -C <sub>14</sub> alkyl N-methyl glucamide   |
| TFAA         | : C <sub>16</sub> -C <sub>18</sub> alkyl N-methyl glucamide.  |
| TPKFA        | : C <sub>12</sub> -C <sub>14</sub> topped whole cut fatty acids.  |
| DEQA         | : Di-(tallow-oxy-ethyl) dimethyl ammonium chloride.   |
| SDASA        | : 1:2 ratio of stearyl dimethyl amine:triple-pressed stearic acid.  |
| Neodol 45-13 | : C <sub>14</sub> -C <sub>15</sub> linear primary alcohol ethoxylate, sold by Shell Chemical CO.  |
| Tallow       | : Dihydrogenated tallowamidoethyl hydroxyethylmonium methosulfate / glycol distearate / cetyl alcohol.  |
| Silicate     | : Amorphous Sodium Silicate (SiO <sub>2</sub> :Na <sub>2</sub> O ratio = 2.0)   |
| NaSKS-6      | : Crystalline layered silicate of formula $\delta$ -Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> .  |

- Carbonate : Anhydrous sodium carbonate with a particle size between 200  $\mu\text{m}$  and 900 $\mu\text{m}$ .
- Bicarbonate : Anhydrous sodium bicarbonate with a particle size between 400  $\mu\text{m}$  and 1200 $\mu\text{m}$ .
- STPP : Anhydrous sodium tripolyphosphate
- MA/AA : Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 80,000
- PA30 : Polyacrylic acid of average molecular weight of approximately 8,000.
- Terpolymer : Terpolymer of average molecular weight approx. 7,000, comprising acrylic:maleic:ethylacrylic acid monomer units at a weight ratio of 60:20:20
- 480N : Random copolymer of 3:7 acrylic/methacrylic acid, average molecular weight about 3,500.
- Polyacrylate : Polyacrylate homopolymer with an average molecular weight of 8,000 sold under the tradename PA30 by BASF GmbH
- Zeolite A : Hydrated Sodium Aluminosilicate of formula  $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$  having a primary particle size in the range from 0.1 to 10 micrometers

|                       |  |
|-----------------------|--|
| Citrate               | : Tri-sodium citrate dihydrate of activity 86,4% with a particle size distribution between 425 $\mu\text{m}$ and 850 $\mu\text{m}$ . |
| Citric                | : Anhydrous citric acid  |
| PB1                   | : Anhydrous sodium perborate monohydrate bleach, empirical formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$                        |
| PB4                   | : Anhydrous sodium perborate tetrahydrate  |
| Percarbonate          | : Anhydrous sodium percarbonate bleach of empirical formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$                    |
| TAED                  | : Tetraacetyl ethylene diamine.  |
| NOBS                  | : Nonanoyloxybenzene sulfonate in the form of the sodium salt.   |
| Photoactivated Bleach | : Sulfonated zinc phthalocyanine encapsulated in dextrin soluble polymer.  |
| PAAC                  | : Pentaamine acetate cobalt(III) salt.   |
| Paraffin              | : Paraffin oil sold under the tradename Winog 70 by Wintershall.   |
| BzP                   | : Benzoyl Peroxide.  |
| Mycodextranase        | : 1,3-1,4- $\alpha$ -D-Glucan 4-glucanohydrolase   |

- Protease : Proteolytic enzyme sold under the tradename Savinase, Alcalase, Durazym by Novo Nordisk A/S, Maxacal, Maxapem sold by Gist-Brocades and proteases described in patents WO91/06637 and/or WO95/10591 and/or EP 251 446.
- Amylase : Amylolytic enzyme sold under the tradename Purafact Ox Am<sup>R</sup> described in WO 94/18314, WO96/05295 sold by Genencor; Termamyl<sup>®</sup>, Fungamyl<sup>®</sup> and Duramyl<sup>®</sup>, all available from Novo Nordisk A/S and those described in WO95/26397.
- Lipase : Lipolytic enzyme sold under the tradename Lipolase, Lipolase Ultra by Novo Nordisk A/S
- Cellulase : Cellulytic enzyme sold under the tradename Carezyme, Celluzyme and/or Endolase by Novo Nordisk A/S.
- CMC : Sodium carboxymethyl cellulose.
- HEDP : 1,1-hydroxyethane diphosphonic acid.
- DETPMP : Diethylene triamine penta (methylene phosphonic acid), marketed by Monsanto under the Trade name Dequest 2060.
- PVNO : Poly(4-vinylpyridine)-N-Oxide.
- PVPVI : Poly (4-vinylpyridine)-N-oxide/copolymer of vinyl-imidazole and vinyl-pyrrolidone.

|                          |  |
|--------------------------|--|
| Brightener 1             | : Disodium 4,4'-bis(2-sulphostyryl)biphenyl.   |
| Brightener 2             | : Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl) stilbene-2:2'-disulfonate.  |
| Silicone antifoam        | : Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1. |
| Granular Suds Suppressor | : 12% Silicone/silica, 18% stearyl alcohol, 70% starch in granular form  |
| SRP 1                    | : Sulfobenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone.  |
| SRP 2                    | : Diethoxylated poly (1,2 propylene terephthalate) short block polymer.  |
| SCS                      | : Sodium cumene sulphonate   |
| Sulfate                  | : Anhydrous sodium sulfate.  |
| HMWPEO                   | : High molecular weight polyethylene oxide   |
| PEG                      | : Polyethylene glycol.   |
| BTA                      | : Benzotriazole  |
| Bismuth nitrate          | : Bismuth nitrate salt   |
| NaDCC                    | : Sodium dichloroisocyanurate  |

Encapsulated : Insoluble fragrance delivery technology  
perfume : utilising zeolite 13x, perfume and a  
particles : dextrose/glycerin agglomerating binder.

KOH : 100% Active solution of Potassium  
Hydroxide

Silica dental : Precipitated silica identified as Zeodent  
abrasive : 119 offered by J.M. Huber.

Carboxyvinyl : Carbopol offered by B.F. Goodrich Chemical  
polymer : Company.

Carrageenan : Iota Carrageenan offered by Hercules  
Chemical Company.

pH : Measured as a 1% solution in distilled  
water at 20°C.

Example 1

The following laundry detergent compositions were prepared in accord with the invention:

5

|                                | I      | II     | III    | IV     | V      | VI     |
|--------------------------------|--------|--------|--------|--------|--------|--------|
| LAS                            | 8.0    | 8.0    | 8.0    | 8.0    | 8.0    | 8.0    |
| C25E3                          | 3.4    | 3.4    | 3.4    | 3.4    | 3.4    | 3.4    |
| QAS                            | -      | 0.8    | 0.8    | -      | 0.8    | 0.8    |
| Zeolite A                      | 18.1   | 18.1   | 18.1   | 18.1   | 18.1   | 18.1   |
| Carbonate                      | 13.0   | 13.0   | 13.0   | 27.0   | 27.0   | 27.0   |
| Silicate                       | 1.4    | 1.4    | 1.4    | 3.0    | 3.0    | 3.0    |
| Sulfate                        | 26.1   | 26.1   | 26.1   | 26.1   | 26.1   | 26.1   |
| PB4                            | 9.0    | 9.0    | 9.0    | 9.0    | 9.0    | 9.0    |
| TAED                           | 1.5    | 1.5    | 1.5    | 1.5    | 1.5    | 1.5    |
| DETPMP                         | 0.25   | 0.25   | 0.25   | 0.25   | 0.25   | 0.25   |
| HEDP                           | 0.3    | 0.3    | 0.3    | 0.3    | 0.3    | 0.3    |
| Mycodextranase                 | 0.001  | 0.001  | 0.003  | 0.001  | 0.001  | 0.003  |
| Protease                       | 0.0026 | 0.0026 | 0.0026 | 0.0026 | 0.0026 | 0.0026 |
| Amylase                        | -      | 0.0009 | 0.0009 | 0.0009 | 0.0009 | 0.0009 |
| MA/AA                          | 0.3    | 0.3    | 0.3    | 0.3    | 0.3    | 0.3    |
| CMC                            | 0.2    | 0.2    | 0.2    | 0.2    | 0.2    | 0.2    |
| Photoactivated<br>bleach (ppm) | 15     | 15     | 15     | 15     | 15     | 15     |
| Brightener 1                   | 0.09   | 0.09   | 0.09   | 0.09   | 0.09   | 0.09   |
| Perfume                        | 0.3    | 0.3    | 0.3    | 0.3    | 0.3    | 0.3    |
| Silicone                       | 0.5    | 0.5    | 0.5    | 0.5    | 0.5    | 0.5    |
| antifoam                       |        |        |        |        |        |        |
| Misc/minors to 100%            |        |        |        |        |        |        |
| Density in<br>g/litre          | 850    | 850    | 850    | 850    | 850    | 850    |

Example 2

5 The following granular laundry detergent compositions of bulk density 750 g/litre were prepared in accord with the invention:

|                                   | I      | II     | III    |
|-----------------------------------|--------|--------|--------|
| LAS                               | 5.25   | 5.61   | 4.76   |
| TAS                               | 1.25   | 1.86   | 1.57   |
| C45AS                             | -      | 2.24   | 3.89   |
| C25AE3S                           | -      | 0.76   | 1.18   |
| C45E7                             | 3.25   | -      | 5.0    |
| C25E3                             | -      | 5.5    | -      |
| QAS                               | 0.8    | 2.0    | 2.0    |
| STPP                              | 19.7   | -      | -      |
| Zeolite A                         | -      | 19.5   | 19.5   |
| NaSKS-6/citric acid<br>(79:21)    | -      | 10.6   | 10.6   |
| Carbonate                         | 6.1    | 21.4   | 21.4   |
| Bicarbonate                       | -      | 2.0    | 2.0    |
| Silicate                          | 6.8    | -      | -      |
| Sodium sulfate                    | 39.8   | -      | 14.3   |
| PB4                               | 5.0    | 12.7   | -      |
| TAED                              | 0.5    | 3.1    | -      |
| DETPMP                            | 0.25   | 0.2    | 0.2    |
| HEDP                              | -      | 0.3    | 0.3    |
| Mycodextranase                    | 0.001  | 0.001  | 0.001  |
| Protease                          | 0.0026 | 0.0085 | 0.045  |
| Lipase                            | 0.003  | 0.003  | 0.003  |
| Cellulase                         | 0.0006 | 0.0006 | 0.0006 |
| Amylase                           | 0.0009 | 0.0009 | 0.0009 |
| MA/AA                             | 0.8    | 1.6    | 1.6    |
| CMC                               | 0.2    | 0.4    | 0.4    |
| Photoactivated<br>bleach (ppm)    | 15 ppm | 27 ppm | 27 ppm |
| Brightener 1                      | 0.08   | 0.19   | 0.19   |
| Brightener 2                      | -      | 0.04   | 0.04   |
| Encapsulated perfume<br>particles | 0.3    | 0.3    | 0.3    |
| Silicone antifoam                 | 0.5    | 2.4    | 2.4    |
| Minors/misc to 100%               |        |        |        |



Example 3

The following detergent formulations, according to the present invention were prepared, where I is a phosphorus-containing detergent composition, II is a zeolite-containing detergent composition and III is a compact detergent composition:

|                                    | I     | II    | III   |
|------------------------------------|-------|-------|-------|
| Blown Powder                       |       |       |       |
| STPP                               | 24.0  | -     | 24.0  |
| Zeolite A                          | -     | 24.0  | -     |
| C45AS                              | 9.0   | 6.0   | 13.0  |
| MA/AA                              | 2.0   | 4.0   | 2.0   |
| LAS                                | 6.0   | 8.0   | 11.0  |
| TAS                                | 2.0   | -     | -     |
| Silicate                           | 7.0   | 3.0   | 3.0   |
| CMC                                | 1.0   | 1.0   | 0.5   |
| Brightener 2                       | 0.2   | 0.2   | 0.2   |
| Soap                               | 1.0   | 1.0   | 1.0   |
| DETPMP                             | 0.4   | 0.4   | 0.2   |
| Spray On                           |       |       |       |
| C45E7                              | 2.5   | 2.5   | 2.0   |
| C25E3                              | 2.5   | 2.5   | 2.0   |
| Silicone antifoam                  | 0.3   | 0.3   | 0.3   |
| Perfume                            | 0.3   | 0.3   | 0.3   |
| Dry additives                      |       |       |       |
| Carbonate                          | 6.0   | 13.0  | 15.0  |
| PB4                                | 18.0  | 18.0  | 10.0  |
| PB1                                | 4.0   | 4.0   | 0     |
| TAED                               | 3.0   | 3.0   | 1.0   |
| Photoactivated bleach              | 0.02  | 0.02  | 0.02  |
| Mycodextranase                     | 0.001 | 0.001 | 0.001 |
| Protease                           | 0.01  | 0.01  | 0.01  |
| Lipase                             | 0.009 | 0.009 | 0.009 |
| Amylase                            | 0.002 | 0.003 | 0.001 |
| Dry mixed sodium sulfate           | 3.0   | 3.0   | 5.0   |
| Balance (Moisture & Miscellaneous) | 100.0 | 100.0 | 100.0 |
| Density (g/litre)                  | 630   | 670   | 670   |

Example 4

The following nil bleach-containing detergent formulations of particular use in the washing of colored clothing, according to the present invention were prepared:

|                                      | I     | II    | III   |
|--------------------------------------|-------|-------|-------|
| Blown Powder                         |       |       |       |
| Zeolite A                            | 15.0  | 15.0  | -     |
| Sodium sulfate                       | 0.0   | 5.0   | -     |
| LAS                                  | 3.0   | 3.0   | -     |
| DETPMP                               | 0.4   | 0.5   | -     |
| CMC                                  | 0.4   | 0.4   | -     |
| MA/AA                                | 4.0   | 4.0   | -     |
| Agglomerates                         |       |       |       |
| C45AS                                | -     | -     | 11.0  |
| LAS                                  | 6.0   | 5.0   | -     |
| TAS                                  | 3.0   | 2.0   | -     |
| Silicate                             | 4.0   | 4.0   | -     |
| Zeolite A                            | 10.0  | 15.0  | 13.0  |
| CMC                                  | -     | -     | 0.5   |
| MA/AA                                | -     | -     | 2.0   |
| Carbonate                            | 9.0   | 7.0   | 7.0   |
| Spray On                             |       |       |       |
| Perfume                              | 0.3   | 0.3   | 0.5   |
| C45E7                                | 4.0   | 4.0   | 4.0   |
| C25E3                                | 2.0   | 2.0   | 2.0   |
| Dry additives                        |       |       |       |
| MA/AA                                | -     | -     | 3.0   |
| NaSKS-6                              | -     | -     | 12.0  |
| Citrate                              | 10.0  | -     | 8.0   |
| Bicarbonate                          | 7.0   | 3.0   | 5.0   |
| Carbonate                            | 8.0   | 5.0   | 7.0   |
| PVPVI/PVNO                           | 0.5   | 0.5   | 0.5   |
| Mycodextranase                       | 0.1   | 0.1   | 0.1   |
| Protease                             | 0.026 | 0.016 | 0.047 |
| Lipase                               | 0.009 | 0.009 | 0.009 |
| Amylase                              | 0.005 | 0.005 | 0.005 |
| Cellulase                            | 0.006 | 0.006 | 0.006 |
| Silicone antifoam                    | 5.0   | 5.0   | 5.0   |
| Dry additives                        |       |       |       |
| Sodium sulfate                       | 0.0   | 9.0   | 0.0   |
| Balance (Moisture and Miscellaneous) | 100.0 | 100.0 | 100.0 |

**WO 98/13457**

**PCT/US96/15572**

64

Density (g/litre)

700

700

700

Example 5

The following detergent formulations, according to the present invention were prepared:

5

|  | I      | II     | III   | IV    |
|--|--------|--------|-------|-------|
| LAS  | 20.0   | 14.0   | 24.0  | 22.0  |
| QAS  | 0.7    | 1.0    | -     | 0.7   |
| TFAA                                       | -      | 1.0    | -     | -     |
| C25E5/C45E7                                | -      | 2.0    | -     | 0.5   |
| C45E3S                                     | -      | 2.5    | -     | -     |
| STPP                                       | 30.0   | 18.0   | 30.0  | 22.0  |
| Silicate                                   | 9.0    | 5.0    | 10.0  | 8.0   |
| Carbonate                                  | 13.0   | 7.5    | -     | 5.0   |
| Bicarbonate                                | -      | 7.5    | -     | -     |
| DETPMP                                     | 0.7    | 1.0    | -     | -     |
| SRP 1                                      | 0.3    | 0.2    | -     | 0.1   |
| MA/AA                                      | 2.0    | 1.5    | 2.0   | 1.0   |
| CMC  | 0.8    | 0.4    | 0.4   | 0.2   |
| Mycodextranase                             | 0.001  | 0.001  | 0.003 | 0.003 |
| Protease                                   | 0.008  | 0.01   | 0.026 | 0.026 |
| Amylase                                    | 0.007  | 0.004  | -     | 0.002 |
| Lipase                                     | 0.004  | 0.002  | 0.004 | 0.002 |
| Cellulase                                  | 0.0015 | 0.0005 | -     | -     |
| Photoactivated<br>bleach (ppm)             | 70ppm  | 45ppm  | -     | 10ppm |
| Brightener 1                               | 0.2    | 0.2    | 0.08  | 0.2   |
| PB1  | 6.0    | 2.0    | -     | -     |
| NOBS                                       | 2.0    | 1.0    | -     | -     |
| Balance<br>(Moisture and<br>Miscellaneous) | 100    | 100    | 100   | 100   |

Example 6

The following detergent formulations, according to the present invention were prepared:

5

|   | I      | II     | III    | IV            |
|---|--------|--------|--------|---------------|
| Blown Powder                            |        |        |        |               |
| Zeolite A                               | 30.0   | 22.0   | 6.0    | 6.7           |
| Na SkS-6                                | -      | -      | -      | 3.3           |
| Polycarboxylate                         | -      | -      | -      | 7.1           |
| Sodium sulfate                          | 19.0   | 5.0    | 7.0    | -             |
| MA/AA                                   | 3.0    | 3.0    | 6.0    | -             |
| LAS                                     | 14.0   | 12.0   | 22.0   | 21.5          |
| C45AS                                   | 8.0    | 7.0    | 7.0    | 5.5           |
| Cationic                                | -      | -      | -      | 1.0           |
| Silicate                                | -      | 1.0    | 5.0    | 11.4          |
| Soap                                    | -      | -      | 2.0    | -             |
| Brightener 1                            | 0.2    | 0.2    | 0.2    | -             |
| Carbonate                               | 8.0    | 16.0   | 20.0   | 10.0          |
| DETPMP                                  | -      | 0.4    | 0.4    | -             |
| Spray On                                |        |        |        |               |
| C45E7                                   | 1.0    | 1.0    | 1.0    | 3.2           |
| Dry additives                           |        |        |        |               |
| PVPVI/PVNO                              | 0.5    | 0.5    | 0.5    | -             |
| Mycodextranase                          | 0.07   | 0.1    | 0.07   | 0.1           |
| Protease                                | 0.052  | 0.01   | 0.01   | 0.01          |
| Lipase                                  | 0.009  | 0.009  | 0.009  | 0.009         |
| Amylase                                 | 0.001  | 0.001  | 0.001  | 0.001         |
| Cellulase                               | 0.0002 | 0.0002 | 0.0002 | 0.0002        |
| NOBS                                    | -      | 6.1    | 4.5    | 3.2           |
| PB1                                     | 1.0    | 5.0    | 6.0    | 3.9           |
| Sodium sulfate                          | -      | 6.0    | -      | to<br>balance |
| Balance (Moisture<br>and Miscellaneous) | 100    | 100    | 100    |               |

Example 7

The following high density and bleach-containing detergent formulations, according to the present invention were  
 5 prepared:

|                                       | I     | II    | III   |
|---------------------------------------|-------|-------|-------|
| Blown Powder                          |       |       |       |
| Zeolite A                             | 15.0  | 15.0  | 15.0  |
| Sodium sulfate                        | 0.0   | 5.0   | 0.0   |
| LAS                                   | 3.0   | 3.0   | 3.0   |
| QAS                                   | -     | 1.5   | 1.5   |
| DETPMP                                | 0.4   | 0.4   | 0.4   |
| CMC                                   | 0.4   | 0.4   | 0.4   |
| MA/AA                                 | 4.0   | 2.0   | 2.0   |
| Agglomerates                          |       |       |       |
| LAS                                   | 5.0   | 5.0   | 5.0   |
| TAS                                   | 2.0   | 2.0   | 1.0   |
| Silicate                              | 3.0   | 3.0   | 4.0   |
| Zeolite A                             | 8.0   | 8.0   | 8.0   |
| Carbonate                             | 8.0   | 8.0   | 4.0   |
| Spray On                              |       |       |       |
| Perfume                               | 0.3   | 0.3   | 0.3   |
| C45E7                                 | 2.0   | 2.0   | 2.0   |
| C25E3                                 | 2.0   | -     | -     |
| Dry additives                         |       |       |       |
| Citrate                               | 5.0   | -     | 2.0   |
| Bicarbonate                           | -     | 3.0   | -     |
| Carbonate                             | 8.0   | 15.0  | 10.0  |
| TAED                                  | 6.0   | 2.0   | 5.0   |
| PB1                                   | 14.0  | 7.0   | 10.0  |
| Polyethylene oxide of MW<br>5,000,000 | -     | -     | 0.2   |
| Bentonite clay                        | -     | -     | 10.0  |
| Mycodextranase                        | 0.001 | 0.001 | 0.001 |
| Protease                              | 0.01  | 0.01  | 0.01  |
| Lipase                                | 0.009 | 0.009 | 0.009 |
| Amylase                               | 0.005 | 0.005 | 0.005 |
| Cellulase                             | 0.002 | 0.002 | 0.002 |
| Silicone antifoam                     | 5.0   | 5.0   | 5.0   |
| Dry additives                         |       |       |       |
| Sodium sulfate                        | 0.0   | 3.0   | 0.0   |

**WO 98/13457**

**PCT/US96/15572**

68

|   |       |       |       |
|---|-------|-------|-------|
| Balance (Moisture and<br>Miscellaneous) | 100.0 | 100.0 | 100.0 |
| Density (g/litre)                       | 850   | 850   | 850   |

Example 8

The following high density detergent formulations, according to the present invention were prepared:

5

|   | I     | II    |
|---|-------|-------|
| Agglomerate                             |       |       |
| C45AS                                   | 11.0  | 14.0  |
| Zeolite A                               | 15.0  | 6.0   |
| Carbonate                               | 4.0   | 8.0   |
| MA/AA                                   | 4.0   | 2.0   |
| CMC                                     | 0.5   | 0.5   |
| DETPMP                                  | 0.4   | 0.4   |
| Spray On                                |       |       |
| C25E5                                   | 5.0   | 5.0   |
| Perfume                                 | 0.5   | 0.5   |
| Dry Adds                                |       |       |
| HEDP                                    | 0.5   | 0.3   |
| SKS 6                                   | 13.0  | 10.0  |
| Citrate                                 | 3.0   | 1.0   |
| TAED                                    | 5.0   | 7.0   |
| Percarbonate                            | 20.0  | 20.0  |
| SRP 1                                   | 0.3   | 0.3   |
| Mycodextranase                          | 0.001 | 0.003 |
| Protease                                | 0.014 | 0.014 |
| Lipase                                  | 0.009 | 0.009 |
| Cellulase                               | 0.001 | 0.001 |
| Amylase                                 | 0.005 | 0.005 |
| Silicone antifoam                       | 5.0   | 5.0   |
| Brightener 1                            | 0.2   | 0.2   |
| Brightener 2                            | 0.2   | -     |
| Balance (Moisture and<br>Miscellaneous) | 100   | 100   |
| Density (g/litre)                       | 850   | 850   |



Example 9

The following granular detergent formulations, according to the present invention were prepared:

5

|  | I     | II    | III        | IV    | V     |
|--|-------|-------|------------|-------|-------|
| LAS  | 21.0  | 25.0  | 18.0       | 18.0  | -     |
| Coco C12-14 AS                                     | -     | -     | -          | -     | 21.9  |
| AE3S   | -     | -     | 1.5        | 1.5   | 2.3   |
| Decyl dimethyl<br>hydroxyethyl NH <sub>4</sub> +Cl | -     | 0.4   | 0.7        | 0.7   | 0.8   |
| Nonionic   | 1.2   | -     | 0.9        | 0.5   | -     |
| Coco C12-14 Fatty                                  | -     | -     | -          | -     | 1.0   |
| Alcohol  |       |       |            |       |       |
| STPP   | 44.0  | 25.0  | 22.5       | 22.5  | 22.5  |
| Zeolite A  | 7.0   | 10.0  | -          | -     | 8.0   |
| MA/AA  | -     | -     | 0.9        | 0.9   | -     |
| SRP1   | 0.3   | 0.15  | 0.2        | 0.1   | 0.2   |
| CMC  | 0.3   | 2.0   | 0.75       | 0.4   | 1.0   |
| Carbonate  | 17.5  | 29.3  | 5.0        | 13.0  | 15.0  |
| Silicate   | 2.0   | -     | 7.6        | 7.9   | -     |
| Mycodextranase                                     | 0.003 | 0.001 | 0.001      | 0.003 | 0.003 |
| Protease   | 0.007 | 0.007 | 0.007      | 0.007 | 0.007 |
| Amylase  | -     | 0.004 | 0.004      | 0.004 | 0.004 |
| Lipase   | 0.003 | 0.003 | 0.003      | -     | -     |
| Cellulase  | -     | 0.001 | 0.001      | 0.001 | 0.001 |
| NOBS   | -     | -     | -          | 1.2   | 1.0   |
| PB1  | -     | -     | -          | 2.4   | 1.2   |
| Diethylene triamine                                | -     | -     | -          | 0.7   | 1.0   |
| penta acetic acid                                  |       |       |            |       |       |
| Diethylene triamine                                | -     | -     | 0.6        | -     | -     |
| penta methyl<br>phosphonic acid                    |       |       |            |       |       |
| Mg Sulfate   | -     | -     | 0.8        | -     | -     |
| Photoactivated bleach                              | 45    | 50    | 15         | 45    | 42    |
|  | ppm   | ppm   | ppm        | ppm   | ppm   |
| Brightener 1                                       | 0.05  | -     | 0.04       | 0.04  | 0.04  |
| Brightener 2                                       | 0.1   | 0.3   | 0.05       | 0.13  | 0.13  |
| Water and Minors                                   |       |       | up to 100% |       |       |

Example 10

The following liquid detergent formulations, according to the present invention were prepared:

5

|                                      | I    | II    | III  | IV    | V    | VI   | VII   | VIII  |
|--------------------------------------|------|-------|------|-------|------|------|-------|-------|
| LAS                                  | 10.0 | 13.0  | 9.0  | -     | 25.0 | -    | -     | -     |
| C25AS                                | 4.0  | 1.0   | 2.0  | 10.0  | -    | 13.0 | 18.0  | 15.0  |
| C25E3S                               | 1.0  | -     | -    | 3.0   | -    | 2.0  | 2.0   | 4.0   |
| C25E7                                | 6.0  | 8.0   | 13.0 | 2.5   | -    | -    | 4.0   | 4.0   |
| TFAA                                 | -    | -     | -    | 4.5   | -    | 6.0  | 8.0   | 8.0   |
| QAS                                  | -    | -     | -    | -     | 3.0  | 1.0  | -     | -     |
| TPKFA                                | 2.0  | -     | 13.0 | 2.0   | -    | 15.0 | 7.0   | 7.0   |
| Rapeseed fatty acids                 | -    | -     | -    | 5.0   | -    | -    | 4.0   | 4.0   |
| Citric                               | 2.0  | 3.0   | 1.0  | 1.5   | 1.0  | 1.0  | 1.0   | 1.0   |
| Dodecenyl/tetradecenyl succinic acid | 12.0 | 10.0  | -    | -     | 15.0 | -    | -     | -     |
| Oleic acid                           | 4.0  | 2.0   | 1.0  | -     | 1.0  | -    | -     | -     |
| Ethanol                              | 4.0  | 4.0   | 7.0  | 2.0   | 7.0  | 2.0  | 3.0   | 2.0   |
| 1,2 Propanediol                      | 4.0  | 4.0   | 2.0  | 7.0   | 6.0  | 8.0  | 10.0  | 13.0  |
| Mono Ethanol Amine                   | -    | -     | -    | 5.0   | -    | -    | 9.0   | 9.0   |
| Tri Ethanol Amine                    | -    | -     | 8    | -     | -    | -    | -     | -     |
| NaOH (pH)                            | 8.0  | 8.0   | 7.6  | 7.7   | 8.0  | 7.5  | 8.0   | 8.2   |
| Ethoxylated tetraethylene pentamine  | 0.5  | -     | 0.5  | 0.2   | -    | -    | 0.4   | 0.3   |
| DETPMP                               | 1.0  | 1.0   | 0.5  | 1.0   | 2.0  | 1.2  | 1.0   | -     |
| SRP 2                                | 0.3  | -     | 0.3  | 0.1   | -    | -    | 0.2   | 0.1   |
| PVNO                                 | -    | -     | -    | -     | -    | -    | -     | 0.10  |
| Mycodextranase                       | 0.1  | 0.1   | 0.1  | 0.07  | 0.1  | 0.1  | 0.07  | 0.07  |
| Protease                             | .005 | .005  | .004 | .003  | 0.08 | .005 | .003  | .006  |
| Lipase                               | -    | .002  | -    | .0002 | -    | -    | .003  | .003  |
| Amylase                              | .002 | .002  | .005 | .004  | .002 | .008 | .005  | .005  |
| Cellulase                            | -    | -     | -    | .0001 | -    | -    | .0004 | .0004 |
| Boric acid                           | 0.1  | 0.2   | -    | 2.0   | 1.0  | 1.5  | 2.5   | 2.5   |
| Na formate                           | -    | -     | 1.0  | -     | -    | -    | -     | -     |
| Ca chloride                          | -    | 0.015 | -    | 0.01  | -    | -    | -     | -     |
| Bentonite clay                       | -    | -     | -    | -     | 4.0  | 4.0  | -     | -     |
| Suspending clay                      | -    | -     | -    | -     | 0.6  | 0.3  | -     | -     |
| SD3                                  | -    | -     | -    | -     | -    | -    | -     | -     |
| Balance                              | 100  | 100   | 100  | 100   | 100  | 100  | 100   | 100   |
| Moisture and Miscellaneous           | -    | -     | -    | -     | -    | -    | -     | -     |

Example 11

Granular fabric cleaning compositions which provide  
 "softening through the wash" capability were prepared in  
 5 accord with the present invention :

|   | I          | II    |
|---|------------|-------|
| 45AS  | -          | 10.0  |
| LAS   | 7.6        | -     |
| 68AS  | 1.3        | -     |
| 45E7  | 4.0        | -     |
| 25E3  | -          | 5.0   |
| Coco-alkyl-dimethyl hydroxy-<br>ethyl ammonium chloride | 1.4        | 1.0   |
| Citrate   | 5.0        | 3.0   |
| Na-SKS-6  | -          | 11.0  |
| Zeolite A   | 15.0       | 15.0  |
| MA/AA   | 4.0        | 4.0   |
| DETPMP  | 0.4        | 0.4   |
| PB1   | 15.0       | -     |
| Percarbonate  | -          | 15.0  |
| TAED  | 5.0        | 5.0   |
| Smectite clay   | 10.0       | 10.0  |
| HMWPEO  | -          | 0.1   |
| Mycodextranase  | 0.001      | 0.001 |
| Protease  | 0.02       | 0.01  |
| Lipase  | 0.02       | 0.01  |
| Amylase   | 0.03       | 0.005 |
| Cellulase   | 0.001      | -     |
| Silicate  | 3.0        | 5.0   |
| Carbonate   | 10.0       | 10.0  |
| Granular suds suppressor                                | 1.0        | 4.0   |
| CMC   | 0.2        | 0.1   |
| Water/minors  | Up to 100% |       |

Example 12

The following rinse added fabric softener composition was prepared in accord with the present invention :

5

|                   |            |
|-------------------|------------|
| Softener active   | 20.0       |
| Mycodextranase    | 0.001      |
| Amylase           | 0.001      |
| Cellulase         | 0.001      |
| HCL               | 0.03       |
| Antifoam agent    | 0.01       |
| Blue dye          | 25ppm      |
| CaCl <sub>2</sub> | 0.20       |
| Perfume           | 0.90       |
| Water / minors    | Up to 100% |

Example 13

10

The following fabric softener composition was prepared in accord with the present invention :

|                      | I      | II     | III  |
|----------------------|--------|--------|------|
| DEQA                 | 2.6    | 19.0   | -    |
| SDASA                | -      | -      | 70.0 |
| Stearic acid of IV=0 | 0.3    | -      | -    |
| Neodol 45-13         | -      | -      | 13.0 |
| Hydrochloride acid   | 0.02   | 0.02   | -    |
| EthanoI              | -      | -      | 1.0  |
| PEG                  | -      | 0.6    | -    |
| Mycodextranase       | 0.1    | 0.1    | 0.05 |
| Perfume              | 1.0    | 1.0    | 0.75 |
| Digeranyl Succinate  | -      | -      | 0.38 |
| Silicone antifoam    | 0.01   | 0.01   | -    |
| Electrolyte          | -      | 600ppm | -    |
| Dye                  | 100ppm | 50ppm  | 0.01 |
| Water and minors     | 100%   | 100%   | 100% |

Example 14

Syndet bar fabric cleaning compositions were prepared in accord with the present invention :

5

|                         | I     | II    | III   | IV    |
|-------------------------|-------|-------|-------|-------|
| C26 AS                  | 20.00 | 20.00 | 20.00 | 20.00 |
| CFAA                    | 5.0   | 5.0   | 5.0   | 5.0   |
| LAS (C11-13)            | 10.0  | 10.0  | 10.0  | 10.0  |
| Sodium carbonate        | 25.0  | 25.0  | 25.0  | 25.0  |
| Sodium pyrophosphate    | 7.0   | 7.0   | 7.0   | 7.0   |
| STPP                    | 7.0   | 7.0   | 7.0   | 7.0   |
| Zeolite A               | 5.0   | 5.0   | 5.0   | 5.0   |
| CMC                     | 0.2   | 0.2   | 0.2   | 0.2   |
| Polyacrylate (MW 1400)  | 0.2   | 0.2   | 0.2   | 0.2   |
| Coconut monethanolamide | 5.0   | 5.0   | 5.0   | 5.0   |
| Mycodextranase          | 0.001 | 0.001 | 0.001 | 0.001 |
| Amylase                 | 0.001 | 0.001 | 0.001 | 0.001 |
| Protease                | 0.03  | -     | 0.05  | 0.005 |
| Brightener, perfume     | 0.2   | 0.2   | 0.2   | 0.2   |
| CaSO <sub>4</sub>       | 1.0   | 1.0   | 1.0   | 1.0   |
| MgSO <sub>4</sub>       | 1.0   | 1.0   | 1.0   | 1.0   |
| Water                   | 4.0   | 4.0   | 4.0   | 4.0   |

Filler\* : balance to 100%

\*Can be selected from convenient materials such as CaCO<sub>3</sub>, talc, clay (Kaolinite, Smectite), silicates, and the like.

Example 15

The following compact high density (0.96Kg/l) dishwashing detergent compositions I to VI were prepared in  
 5 accord with the present invention:

|                  | I     | II    | III   | IV    | V    | VI     |
|------------------|-------|-------|-------|-------|------|--------|
| STPP             | -     | -     | 49.0  | 38.0  | -    | -      |
| Citrate          | 33.0  | 17.5  | -     | -     | 54.0 | 25.4   |
| Carbonate        | -     | 17.5  | -     | 20.0  | 14.0 | 25.4   |
| Silicate         | 33.0  | 14.8  | 20.4  | 14.8  | 14.8 | -      |
| Metasilicate     | -     | 2.5   | 2.5   | -     | -    | -      |
| PB1              | 1.9   | 9.7   | 7.8   | 14.3  | 7.8  | -      |
| PB4              | 8.6   | -     | -     | -     | -    | -      |
| Percarbonate     | -     | -     | -     | -     | -    | 6.7    |
| Nonionic         | 1.5   | 2.0   | 1.5   | 1.5   | 1.5  | 2.6    |
| TAED             | 4.8   | 2.4   | 2.4   | -     | 2.4  | 4.0    |
| HEDP             | 0.8   | 1.0   | 0.5   | -     | -    | -      |
| DETPMP           | 0.6   | 0.6   | -     | -     | -    | -      |
| PAAC             | -     | -     | -     | 0.2   | -    | -      |
| BzP              | -     | -     | -     | 4.4   | -    | -      |
| Paraffin         | 0.5   | 0.5   | 0.5   | 0.5   | 0.5  | 0.2    |
| Mycodextranase   | 0.01  | 0.05  | 0.01  | 0.05  | 0.01 | 0.05   |
| Protease         | 0.075 | 0.05  | 0.10  | 0.10  | 0.08 | 0.01   |
| Lipase           | -     | 0.001 | -     | 0.005 | -    | -      |
| Amylase          | 0.01  | 0.005 | 0.015 | 0.015 | 0.01 | 0.0025 |
| BTA              | 0.3   | 0.3   | 0.3   | 0.3   | 0.3  | -      |
| Bismuth Nitrate  | -     | 0.3   | -     | -     | -    | -      |
| PA30             | 4.0   | -     | -     | -     | -    | -      |
| Terpolymer       | -     | -     | -     | 4.0   | -    | -      |
| 480N             | -     | 6.0   | 2.8   | -     | -    | -      |
| Sulfate          | 7.1   | 20.8  | 8.4   | -     | 0.5  | 1.0    |
| pH (1% solution) | 10.8  | 11.0  | 10.9  | 10.8  | 10.9 | 9.6    |

Example 16

The following granular dishwashing detergent compositions examples I to IV of bulk density 1.02Kg/L were prepared in accord with the present invention :

|                  | I     | II    | III   | IV   | V    | VI    |
|------------------|-------|-------|-------|------|------|-------|
| STPP             | 30.0  | 30.0  | 30.0  | 27.9 | 34.5 | 26.7  |
| Carbonate        | 30.5  | 30.5  | 30.5  | 23.0 | 30.5 | 2.80  |
| Silicate         | 7.4   | 7.4   | 7.4   | 12.0 | 8.0  | 20.3  |
| PB1              | 4.4   | 4.4   | 4.4   | -    | 4.4  | -     |
| NaDCC            | -     | -     | -     | 2.0  | -    | 1.5   |
| Nonionic         | 0.75  | 0.75  | 0.75  | 1.9  | 1.2  | 0.5   |
| TAED             | 1.0   | 1.0   | -     | -    | 1.0  | -     |
| PAAC             | -     | -     | 0.004 | -    | -    | -     |
| BzP              | -     | 1.4   | -     | -    | -    | -     |
| Paraffin         | 0.25  | 0.25  | 0.25  | -    | -    | -     |
| Mycodextranase   | 0.01  | 0.05  | 0.01  | 0.05 | 0.01 | 0.05  |
| Protease         | 0.05  | 0.05  | 0.05  | -    | 0.1  | -     |
| Lipase           | 0.005 | -     | 0.001 | -    | -    | -     |
| Amylase          | 0.003 | 0.001 | 0.01  | 0.02 | 0.01 | 0.015 |
| BTA              | 0.15  | -     | 0.15  | -    | -    | -     |
| Sulfate          | 23.9  | 23.9  | 23.9  | 31.4 | 17.4 | -     |
| pH (1% solution) | 10.8  | 10.8  | 10.8  | 10.7 | 10.7 | 12.3  |

Example 17

The following detergent composition tablets of 25g weight were prepared in accord with the present invention by  
5 compression of a granular dishwashing detergent composition at a pressure of 13KN/cm<sup>2</sup> using a standard 12 head rotary press:

|                  | I     | II    | III   |
|------------------|-------|-------|-------|
| STPP             | -     | 48.8  | 47.5  |
| Citrate          | 26.4  | -     | -     |
| Carbonate        | -     | 5.0   | -     |
| Silicate         | 26.4  | 14.8  | 25.0  |
| Mycodextranase   | 0.01  | 0.05  | 0.01  |
| Protease         | 0.03  | 0.075 | 0.01  |
| Lipase           | 0.005 | -     | -     |
| Amylase          | 0.01  | 0.005 | 0.001 |
| PB1              | 1.6   | 7.8   | -     |
| PB4              | 6.9   | -     | 11.4  |
| Nonionic         | 1.2   | 2.0   | 1.1   |
| TAED             | 4.3   | 2.4   | 0.8   |
| HEDP             | 0.7   | -     | -     |
| DETPMP           | 0.65  | -     | -     |
| Paraffin         | 0.4   | 0.5   | -     |
| BTA              | 0.2   | 0.3   | -     |
| PA30             | 3.2   | -     | -     |
| Sulfate          | 25.0  | 14.7  | 3.2   |
| pH (1% solution) | 10.6  | 10.6  | 11.0  |



Example 18

The following liquid dishwashing detergent compositions were prepared in accord with the present invention I to II, of density 1.40Kg/L :

|                  | I     | II     |
|------------------|-------|--------|
| STPP             | 33.3  | 20.0   |
| Carbonate        | 2.7   | 2.0    |
| Silicate         | -     | 4.4    |
| NaDCC            | 1.1   | 1.15   |
| Nonionic         | 2.5   | 1.0    |
| Paraffin         | 2.2   | -      |
| Mycodextranase   | 0.01  | 0.01   |
| Protease         | 0.03  | 0.02   |
| Amylase          | 0.005 | 0.0025 |
| 480N             | 0.50  | 4.00   |
| KOH              | -     | 6.00   |
| Sulfate          | 1.6   | -      |
| pH (1% solution) | 9.1   | 10.0   |

Example 19

The following liquid hard surface cleaning compositions were prepared in accord with the present invention :

|                         | I               | II    | III   | IV    | V     | VI    |
|-------------------------|-----------------|-------|-------|-------|-------|-------|
| Mycodextranase          | 0.001           | 0.005 | 0.001 | 0.005 | 0.001 | 0.005 |
| Amylase                 | 0.01            | 0.002 | 0.005 | 0.02  | 0.001 | 0.005 |
| Protease                | 0.05            | 0.01  | 0.02  | 0.03  | 0.005 | 0.005 |
| EDTA*                   | -               | -     | 2.90  | 2.90  | -     | -     |
| Citrate                 | -               | -     | -     | -     | 2.90  | 2.90  |
| LAS                     | 1.95            | -     | 1.95  | -     | 1.95  | -     |
| C12 AS                  | -               | 2.20  | -     | 2.20  | -     | 2.20  |
| NaC12(ethoxy)           | -               | 2.20  | -     | 2.20  | -     | 2.20  |
| **sulfate               | -               | -     | -     | -     | -     | -     |
| C12 Dimethylamine oxide | -               | 0.50  | -     | 0.50  | -     | 0.50  |
| SCS                     | 1.30            | -     | 1.30  | -     | 1.30  | -     |
| Hexyl Carbitol**        | 6.30            | 6.30  | 6.30  | 6.30  | 6.30  | 6.30  |
| Water                   | Balance to 100% |       |       |       |       |       |

\*Na4 ethylenediamine diacetic acid

15 \*\*Diethylene glycol monohexyl ether

\*\*\*All formulas adjusted to pH 7

Example 20

The following spray composition for cleaning of hard surfaces and removing household mildew was prepared in  
5 accord with the present invention :

|                        |            |
|------------------------|------------|
| Mycodextranase         | 0.01       |
| Amylase                | 0.01       |
| Protease               | 0.01       |
| Sodium octyl sulfate   | 2.00       |
| Sodium dodecyl sulfate | 4.00       |
| Sodium hydroxide       | 0.80       |
| Silicate (Na)          | 0.04       |
| Perfume                | 0.35       |
| Water/minors           | up to 100% |

Example 21

A two-layer effervescent denture cleansing tablet was prepared in accord with the present invention :

5

Acidic Layer

|                           |      |
|---------------------------|------|
| Mycodextranase            | 0.1  |
| Protease                  | 0.1  |
| Tartaric acid             | 24.0 |
| Sodium carbonate          | 4.0  |
| Sulphamic acid            | 10.0 |
| PEG 20,000                | 4.0  |
| Sodium bicarbonate        | 24.5 |
| Potassium persulfate      | 15.0 |
| Sodium acid pyrophosphate | 7.0  |
| Pyrogenic silica          | 2.0  |
| Tetracetylene diamine     | 7.0  |
| Ricin-oleylsulfosuccinate | 0.5  |
| Flavor                    | 1.0  |

Alkaline layer

|                      |      |
|----------------------|------|
| PB1                  | 32.0 |
| Bicarbonate          | 19.0 |
| EDTA                 | 3.0  |
| STPP                 | 12.0 |
| PEG 20,000           | 2.0  |
| Potassium persulfate | 26.0 |
| Sodium carbonate     | 2.0  |
| Pyrogenic silica     | 2.0  |
| Dye/flavor           | 2.0  |

Example 22

Dentifrice compositions were prepared in accord with the present invention :

5

|   | I               | II     | III    | IV     |
|---|-----------------|--------|--------|--------|
| Sorbitol (70% aqueous solution)               | 35.000          | 35.000 | 35.000 | 35.000 |
| PEG-6   | 1.000           | 1.000  | 1.000  | 1.000  |
| Silica dental abrasive                        | 20.000          | 20.000 | 20.000 | 20.000 |
| Sodium fluoride                               | 0.243           | 0.243  | 0.243  | 0.243  |
| Titanium dioxide                              | 0.500           | 0.500  | 0.500  | 0.500  |
| Sodium saccharin                              | 0.286           | 0.286  | 0.286  | 0.286  |
| Mycodextranase                                | 0.5             | 0.5    | 0.3    | 0.3    |
| Protease                                      | 2.000           | 3.500  | 1.500  | 2.000  |
| Sodium alkyl sulfate (27.9% aqueous solution) | 4.000           | 4.000  | 4.000  | 4.000  |
| Flavor  | 1.040           | 1.040  | 1.040  | 1.040  |
| Carboxyvinyl polymer                          | 0.300           | 0.300  | 0.300  | 0.300  |
| Carrageenan                                   | 0.800           | 0.800  | 0.800  | 0.800  |
| Water   | Balance to 100% |        |        |        |

Example 23

10 Mouthwash compositions were prepared in accord with the present invention :

|                  | I               | II    | III   | IV    |
|------------------|-----------------|-------|-------|-------|
| SDA 40 Alcohol   | 8.00            | 8.00  | 8.00  | 8.00  |
| Flavor           | 0.08            | 0.08  | 0.08  | 0.08  |
| Emulsifier       | 0.08            | 0.08  | 0.08  | 0.08  |
| Sodium fluoride  | 0.05            | 0.05  | 0.05  | 0.05  |
| Glycerin         | 10.00           | 10.00 | 10.00 | 10.00 |
| Sweetener        | 0.02            | 0.02  | 0.02  | 0.02  |
| Mycodextranase   | 0.5             | 0.3   | 0.5   | 0.3   |
| Protease         | 3.00            | 7.50  | 1.00  | 5.00  |
| Benzoic acid     | 0.05            | 0.05  | 0.05  | 0.05  |
| Sodium hydroxide | 0.20            | 0.20  | 0.20  | 0.20  |
| Dye              | 0.04            | 0.04  | 0.04  | 0.04  |
| Water            | Balance to 100% |       |       |       |

Example 24

A liquid personal cleansing composition containing soap was prepared in accord with the present invention :

5

|                            | I          | II   |
|----------------------------|------------|------|
| Mycodextranase             | 0.1        | 0.1  |
| Protease                   | 0.10       | -    |
| Soap (K or Na)             | 15.00      | -    |
| 30% Laurate                |            | -    |
| 30% Myristate              |            | -    |
| 25% Palmitate              |            | -    |
| 15% Stearate               |            | -    |
| Fatty acids (above ratios) | 4.50       | -    |
| Na Lauryl Sarcosinate      | 6.00       | -    |
| Sodium Laureth Sulfate     | 0.66       | 12.0 |
| Cocamidopropylbetaine      | 1.33       | 3.0  |
| Glycerine                  | 15.00      | -    |
| Propylene Glycol           | 9.00       | -    |
| Ethylene glycol distearate | 1.50       | 0.38 |
| (EDTA)                     |            |      |
| Cocoamide MEA              | -          | 0.2  |
| Perfume                    | -          | 0.6  |
| *Polyquaterium-7           | -          | 0.08 |
| DMDM hydantoin             | -          | 0.14 |
| Sodium benzoate            | -          | 0.25 |
| Tetrasodium EDTA dihydrate | -          | 0.11 |
| Citric                     | -          | 0.09 |
| Propylparaben              | 0.10       | -    |
| Methylparaben              | 0.20       | -    |
| Calcium sulfate            | 3          | -    |
| Acetic acid                | 3          | -    |
| Water and minors           | Up to 100% |      |
| KOH/NaOH (pH adjustment)   |            |      |

\* Copolymer of dimethyl dialkyl ammonium chloride and  
acrylamide

Example 25

A personal cleansing bar composition was prepared in accord with the present invention :

5

|                                 |                |
|---------------------------------|----------------|
| Sodium Cocoyl Isethionate       | 47.20          |
| Sodium Cetearyl sulfate         | 9.14           |
| Paraffin                        | 9.05           |
| Sodium Soap (in situ)           | 3.67           |
| Sodium Isethionate              | 5.51           |
| Sodium Chloride                 | 0.45           |
| Titanium Dioxide                | 0.4            |
| Trisodium EDTA                  | 0.1            |
| Trisodium Etidronate            | 0.1            |
| Perfume                         | 1.20           |
| Na <sub>2</sub> SO <sub>4</sub> | 0.87           |
| Mycodextranase                  | 0.5            |
| Protease                        | 0.10           |
| Water                           | Balance to 100 |



Example 26

A shampoo composition was prepared in accord with the present invention :

5

|                                   | I          | II   | III  | IV   | V    | VI   |
|-----------------------------------|------------|------|------|------|------|------|
| NH <sub>4</sub> laureth-3 sulfate | 16.0       | 18.0 | 10.0 | 16.0 | 14.0 | 18.0 |
| NH <sub>4</sub> lauryl sulfate    | 5.0        | 6.0  | 3.0  | 3.0  | 4.0  | 6.0  |
| Na lauryl sarcosinate             | -          | -    | 2.0  | -    | -    | -    |
| Cocoamide MEA                     | 1.0        | -    | -    | 1.0  | 0.6  | -    |
| Dimethicone 40/60                 | 0.8        | 1.0  | 0.4  | 3.0  | 2.0  | 1.0  |
| Polyquaternium-10                 | -          | -    | 0.01 | -    | 0.2  | -    |
| Cetyl alcohol                     | 0.5        | 0.4  | -    | 0.4  | 0.4  | 0.1  |
| Stearyl alcohol                   | -          | 0.2  | -    | 0.5  | 0.1  | 0.2  |
| Panthenyl ethyl ether             | 0.2        | -    | -    | 0.2  | 0.2  | 0.2  |
| Panthenol 10%                     | -          | 0.03 | -    | 0.03 | -    | -    |
| Tallow                            | -          | -    | -    | -    | -    | 0.5  |
| Mineral oil                       | -          | -    | -    | -    | 0.5  | -    |
| Tetrasodium EDTA                  | 0.09       | 0.09 | 0.07 | 0.09 | 0.09 | 0.09 |
| DMDM Hydantoin                    | 0.14       | 0.14 | 0.14 | 0.12 | 0.14 | 0.14 |
| Sodium benzoate                   | 0.25       | 0.25 | -    | 0.25 | 0.25 | 0.25 |
| Citrate                           | 1.0        | -    | -    | 1.0  | 1.0  | -    |
| Citric                            | 0.1        | -    | 0.3  | 0.1  | -    | -    |
| Sodium hydroxide                  | -          | -    | 0.3  | -    | -    | -    |
| Sodium phosphate                  | -          | 0.6  | -    | -    | -    | 0.6  |
| Disodium phosphate                | -          | 0.2  | -    | -    | -    | 0.2  |
| Sodium chloride                   | 1.5        | 1.5  | 3.0  | 1.5  | 2.0  | 1.5  |
| PEG-12                            | -          | -    | 0.15 | -    | -    | 0.4  |
| NH <sub>4</sub> xylene sulfonate  | 0.4        | 0.4  | -    | 0.4  | 0.4  | 0.4  |
| Glycol distearate                 | 1.0        | 3.0  | 1.5  | 2.0  | 3.0  | 0.5  |
| Zinc pyrithione                   | -          | -    | 1.0  | -    | -    | -    |
| Mycodextranase                    | 0.05       | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| Perfume                           | 0.2        | 0.6  | 0.6  | 0.2  | 0.4  | 0.6  |
| Water and minors                  | Up to 100% |      |      |      |      |      |

What is claimed is:

1. A cleaning composition comprising a mycodextranase enzyme.
2. The cleaning composition according to Claim 1, wherein said mycodextranase enzyme is present at a level of from about 0.00001% to about 1% as a pure enzyme by weight of composition.
3. The cleaning composition according to Claim 1 further comprising one or more enzymes selected from the group consisting of protease, lipase, cellulase, amylase, and the like.
4. The cleaning composition according to Claim 1 further comprising one or more surfactants selected from the group consisting of nonionic, anionic, cationic, zwitterionic, amphoteric or mixtures thereof.
- 5 5. The cleaning composition according to Claim 1 further comprising one or more components selected from the group consisting of bleaching agents, suds suppressors, soil suspension and anti-redeposition agents, soil release polymer, smectite clays, builder components and the like.
6. The cleaning composition according to Claim 1 characterized in that said composition is in the liquid, paste, gel, bar, tablet, powder or granular form.
7. The cleaning composition according to Claim 1 characterized in that the composition further comprises no more than about 15% by weight of inorganic filler salt.

8. The cleaning composition according to Claim 1 characterized in that the composition is a heavy duty liquid detergent composition.

9. A detergent additive comprising a mycodextranase enzyme.

10. Use of a cleaning composition according to claims 1 to 5 for fabric cleaning and/or fabric stain removal and/or fabric whiteness maintenance and/or fabric softening and/or fabric color appearance and/or fabric dye transfer  
5 inhibition.

11. Use of a cleaning composition according to claims 1 to 5 for cleaning hard surfaces such as floors, walls, bathroom tile and the like.

12. Use of a cleaning composition according to claims 1 to 5 for hand and machine dishwashing.

13. Use of a cleaning composition according to claims 1 to 5 for oral, dental, contact lenses and personal cleaning applications.

14. A detergent composition comprising:

(a) from about 0.1% to about 60% detergent surfactant selected from the group consisting of nonionic, anionic, cationic, zwitterionic, amphoteric surfactant, and mixtures  
5 thereof, by weight of composition;

(b) from about 0.00001% to about 1% pure mycodextranase enzyme by weight of composition; and

(c) no more than about 15% by weight of inorganic filler salt.

10

15. The detergent composition according to Claim 14, comprising:

(a) from about 1% to about 35% detergent surfactant selected from the group consisting of nonionic, anionic, cationic, zwitterionic, amphoteric surfactant, and mixtures thereof, by weight of composition;

(b) from about 0.0001% to about 0.5% pure mycodextranase enzyme by weight of composition; and

(c) one or more components selected from the group consisting of bleaching agents, suds suppressors, soil suspension and anti-redeposition agents, soil release polymer, smectite clays, builder components and the like.

## INTERNATIONAL SEARCH REPORT

International Application No

PC 1/US 96/15572

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C1103/386

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C110

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|------------|---|-----------------------|
| A          | EP 0 425 017 A (THE PROCTER & GAMBLE CO. ;<br>GENENCOR INTERNATIONAL INC. ) 2 May 1991<br>see page 3, line 45 - line 50<br>see page 13, line 25 - line 45<br>see page 17, line 44 - page 18, line 27<br>--- | 1,3-7,<br>10,11,13    |
| A          | US 4 710 313 A (MIYAJIMA NOBUYUKI ET AL.)<br>1 December 1987<br>see abstract<br>---   | 1,3,13                |
| A          | US 4 138 476 A (SIMONSON LLOYD G. ET AL.)<br>6 February 1979<br>see column 3, line 8 - line 34<br>see claims 1,4,11,15,20<br>---  | 1,13                  |
| -/--       |   |                       |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search

28 May 1997

Date of mailing of the international search report

06.06.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

Serbetsoglou, A

# INTERNATIONAL SEARCH REPORT

International Application No  
PC 1/US 96/15572

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
|----------|--|-----------------------|
| A        | <p>CHEMICAL ABSTRACTS, vol. 76, no. 11,<br/>13 March 1972<br/>Columbus, Ohio, US;<br/>abstract no. 55830,<br/>TUNG, K. K. ET AL: "Enzymes that<br/>hydrolyze fungal cell wall<br/>polysaccharides. II. Purification and<br/>properties of mycodetranase, an<br/>endo-.alpha.-D-(1-&gt;4)glucanase from<br/>Penicillium melinii"<br/>XP002031712<br/>cited in the application<br/>see abstract<br/>&amp; J. BIOL. CHEM. (1971), 246(22), 6722-36<br/>CODEN: JBCHA3,<br/>-----</p> | 1                     |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/15572

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|---|---------------------|----------------------------|---------------------|
| EP 0425017 A                              | 02-05-91            | US 5258304 A               | 02-11-93            |
|   |                     | AU 633373 B                | 28-01-93            |
|   |                     | AU 6559490 A               | 02-05-91            |
|   |                     | CA 2028553 A,C             | 28-04-91            |
|   |                     | CN 1052505 A,B             | 26-06-91            |
|   |                     | DE 69024324 D              | 01-02-96            |
|   |                     | DE 69024324 T              | 17-10-96            |
|   |                     | JP 3244696 A               | 31-10-91            |
| -----                                     |                     |                            |                     |
| US 4710313 A                              | 01-12-87            | JP 62000913 A              | 06-01-87            |
| -----                                     |                     |                            |                     |
| US 4138476 A                              | 06-02-79            | NONE                       |                     |
| -----                                     |                     |                            |                     |

BEST AVAILABLE COPY